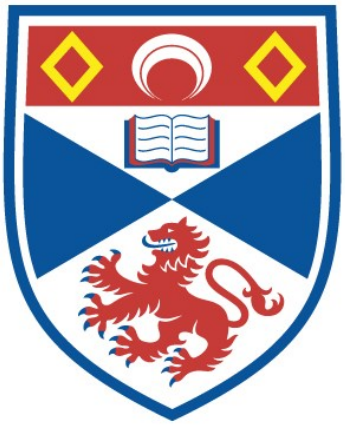
THE PYROLYSIS OF METHYL IODIDE

Robert Kinnear Boyd

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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THE PYROLYSIS OF METHYL IODIDE

A Thesis presented by Robert Kinnear Boyd to the University of St. Andrews in application for the degree of Doctor of Philosophy.

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DECLARATION.

I hereby declare that the following thesis is a record of experiments carried out by me, that the thesis is my own composition, and that it has not been previously presented for a higher degree.

The investigation was carried out in the Chemistry Research Laboratories of St. Salvator's College, St. Andrews, under the supervision of Dr. C. Horrex.

CERTIFICATE

I hereby certify that Robert Kinnear Boyd has spent twelve terms at research work under my supervision, that he has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and that he is qualified to submit the accompanying thesis in application for the degree of Doctor of Philosophy.

UNIVERSITY CAREER

I matriculated in the University of St. Andrews in October, 1955, and graduated B.Sc. with First Class Honours in Chemistry in June 1959.

The work described in this thesis was carried out during the period from September 1959 to September 1962.

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INTRODUCTION

There is an extensive literature on the pyrolysis and photolysis of organic iodides. The main reason for the popularity of these substances as subjects for kinetic investigations is the relative weakness of the carbon-iodine bonds, the comparatively ready splitting of these bonds providing a possible initiating process for the decomposition.

The object of the present work was to establish the kinetics of the pyrolysis of methyl iodide in the presence of hydrogen iodide, with a view to determining the carbon-iodine bond dissociation energy. Ogg[1] carried out a kinetic investigation into the pyrolysis of methyl, ethyl, and n-propyl iodides in the presence of hydrogen iodide. However, apart from the fact that the bond dissociation energies derived from Ogg's analysis of his data are about 12 k.cals. per mole lower than values from other sources, work done in St. Andrews, on the pyrolysis of trifluoromethyl iodide[2] and benzyl iodide[5], suggested that a mechanism different from that postulated by Ogg was operative.

In the light of these considerations, it seemed that a reinvestigation of the thermal reaction between methyl iodide and hydrogen iodide was necessary. Before describing this present work, a summary is given of published work on the decompositions of iodides, and on carbon-iodine bond dissociation energies.

SOME GENERAL FEATURES OF THE PYROLYSES OF ORGANIC COMPOUNDS.

It has been found that the gas-phase pyrolyses of many organic compounds involve free radicals. The existence of free gas-phase radicals was first demonstrated by Paneth and Hofeditz[4] in their study of the decomposition of lead tetramethyl, when they found that the methyl radicals produced removed metallic mirrors.

Some of these free-radical reactions involve a chain mechanism, which can account for the fact that experimentally observed activation energies can be considerably less than any bond-dissociation energy pertaining to the particular compound involved.

The mechanism of the reaction must be completely elucidated in order to allow any elementary reaction rate parameters to be estimated. In free-radical reactions, the precise study of individual reaction steps is hampered by the difficulty of accurately measuring the very small radical concentrations. However, it has been fairly well established that the activation energies for the attack of radicals and atoms on molecules are low.

Besides the activation energy, the other parameter controlling the value of a reaction rate constant is the pre-exponential factor in the Arrhenius expression for the temperature-dependence of the rate constant. The value of k is given by

$$k = A.e^{\frac{-E}{RT}} = p.Z.e^{\frac{-E}{RT}}$$

where E is the activation energy, and Z the collision rate calculated on the basis of the kinetic theory. The steric factor p was introduced to account for temperature- independent factors found to be much smaller than the calculated collision frequency Z. It is supposed to correspond to the fact that, when a free radical approaches a molecule, not only must the energy requirements be satisfied for reaction to occur, but also certain geometrical orientations are necessary for the radical to successfully attack the molecule. This interpretation is borne out to some extent by the fact that the value of p decreases as the complexity of the attacking radical increases. While this general trend holds good, no detailed pattern can be inferred. In fact, attempts to explain the values of p- factors on the basis of kinetic theory are not very successful. A deeper understanding of pre-exponential factors is gained fromtransition state theory, which takes into account the internal degrees of freedom of the reacting species neglected in the classical kinetic theory.

THE DECOMPOSITION OF ORGANIC IODIDES.

When an organic vapour is heated, the weakest bond in the molecule breaks first, since the probability of sufficient energy being concentrated in a bond for this to happen depends on a factor $e^{\frac{-E}{RT}}$. Since the energy required for rupture appears in

the index, a relatively small difference between the dissociation energies of two bonds can mean a large difference between the probabilities of their breaking at a given temperature.

In alkyl iodides, the carbon-iodine bond dissociation energy is the lowest, being about 54 k. cals. per mole. The carbon - carbon and carbon - hydrogen bond energies are of the order of 80 and 100 k. cals. per mole respectively, so that at temperatures where the carbon - iodine link breaks at an experimentally observable rate, the rate of rupture of the other bonds will be negligible. These remarks on the unimolecular fission of bonds also apply, in general, to the relative ease with which the bonds are attacked by other species. Thus, attack by atoms and free radicals will generally consist in preferential attack on the weakest bond in the substrate molecule, although the energy associated with the bond being formed by the reaction also bears on the preferred reaction path. The principal exception to this rule is the phenomenon of hydrogen abstraction by free radicals. The weaker carbon - carbon bonds are not attacked because of the steric shielding provided by the tetrahedral arrangement of atoms around the carbon nuclei.

The primary step in the decomposition of most organic iodides has been deduced from the kinetics as being the breaking of the R - I bond, in accordance with the above. The only other reasonably likely first step is the decomposition into hydrogen iodide and an olefin. This is a much more complicated process than the rupture

of a single carbon - iodine bond, and experimental evidence indicates that it is much less likely to occur than the simple split.

Some iodides, such as methyl, trifluoromethyl, benzyl, and phenyl iodides, cannot decompose to an olefin and HI, since the molecule contains no carbon atom carrying eliminable hydrogen adjacent to the carbon - iodine grouping. For such substances, the only initiating step possible is the rupture of the carbon - iodine linkage. On the other hand, the pyrolysis of t-butyl iodide[5] appears to proceed mainly by the elimination reaction to give isobutylene and hydrogen iodide.

Most other iodides decompose to give a certain amount of HI among the products. This can arise either from the elimination reaction referred to, or from secondary reactions of iodine atoms and the other radical fragments.

For convenience, the possible secondary reactions which can occur will be listed, and the extent to which they have been found to occur then discussed.

When the initiating process consists of the elimination reaction previously described, to give an olefin and HI, the addition of HI to the olefin to reform the parent compound is practically the only conceivable secondary reaction. According to Jones and Ogg,[5] this occurs in the case of t-butyl iodide, an equilibrium being set up.

In the more usual case, where the initial process is bond fission to give a radical R and an iodine atom I, the following processes are conceivable as secondary steps:-

(a) The radical may react with iodine atoms or molecules, to give the parent iodide RI.

(b) The radicals may dimerise, forming R - R, or two radicals can disproportionate to give a saturated hydrocarbon and an olefin.

(c) The radical may decompose by a unimolecular process to give an olefin and a hydrogen atom. This hydrogen atom may then attack either the parent iodide or an iodine molecule, giving rise to HI, plus a radical R or an iodine atom, respectively. Alternatively, the radical may be destroyed on the wall.

(d) The radical may attack an iodide molecule by the process $R + RI \longrightarrow RH + R'$, or even by the step $R + RI \rightarrow R - R + I$. The fragment R' is a radical containing an iodine atom, which may take part in secondary processes analogous to those of the radical R described above.

(e) Iodine atoms will take part in the normal equilibrium

$$I + I\ (+ M) \quad \rightleftharpoons \quad I_2(+ M).$$

(f) An iodine atom may abstract hydrogen from a free radical to give HI plus an olefin.

(g) An iodine atom may attack a parent iodide molecule according to the scheme $I + RI \longrightarrow R + I_2$.

(h) In systems where HI is formed by some process, the reaction of

a radical with HI may take place, thus $R + HI \longrightarrow RH + I$.

Various other conceivable reactions have been omitted from the list. Thus, the reaction $R + HI \longrightarrow RI + H$, being endothermic, is much less likely to occur than (h), which is exothermic. Similarly, the process $I + RI \longrightarrow HI + R^1$, is endothermic by about 29 k. cals. per mole, and is thus much less likely to occur than (g), which is endothermic by about only 19 k. cals. per mole. However, this type of hydrogen abstraction by iodine atoms has been postulated as a step in the iodine-catalysed decomposition of acetone.[6] The hydrogen atoms in this case are rendered labile by the neighbouring carbonyl group, and are thus more liable to be abstracted.

A good example for demonstrating the occurrence of several of these elementary reactions is the photolysis of methyl iodide. It is well known that the quantum yield is extremely low,[7,8] due presumably to the occurrence of highly efficient back reactions. The following mechanism was proposed by West and Schlessinger[9] to account for the kinetics and products identified.

$$CH_3I \xrightarrow{h\nu} CH_3 + I \qquad (1)$$

$$CH_3 + I \longrightarrow CH_3I \qquad (2)$$

$$CH_3 + CH_3I \longrightarrow CH_4 + CH_2I \qquad (3)$$

$$CH_2I + I \longrightarrow CH_2I_2 \qquad (4)$$

$$CH_2I + CH_3 \longrightarrow C_2H_5I \qquad (4a)$$

$$CH_2I + CH_3I \longrightarrow CH_2I_2 + CH_3 \qquad (5)$$

$$CH_2I_2 \xrightarrow{h\nu} CH_2 + I_2 \qquad (6)$$

$$2CH_2 \longrightarrow C_2H_4 \qquad (7)$$

$$CH_2 + CH_3I \longrightarrow C_2H_5I \qquad (8)$$

$$2CH_3 \longrightarrow C_2H_6 \qquad (9)$$

$$I + I + M \longrightarrow I_2 + M \qquad (10)$$

This reaction system is very complicated, and attempts have been made to simplify the kinetics by "fixing" the radicals in some way, thus stopping the secondary reactions. Substances used for this purpose, with varying degrees of success, have been nitric oxide,[10] silver,[9,11,] and hydrogen iodide.[12] It is of some interest that reaction (5) in the above scheme has been postulated as being caused by "hot" methyl radicals.[11,13,14.]

In a series of papers, Ogg and his collaborators have reported the behaviour of a number of iodides on pyrolysis in static systems. The compounds investigated were n-propyl,[15] iso-propyl,[16] n-butyl,[15] sec-butyl,[17] iso-butyl,[18] t-butyl,[5] and ethylene[19] iodides.

The case of t-butyl iodide appears to be exceptional, since, as stated previously, the major part of the reaction appears to involve a direct molecular split, yielding the olefin and HI. The kinetics of the iso-propyl iodide decomposition could be explained on the basis of a similar initiating step, but this mechanism is open to various difficulties in this case, and a free radical mechanism appears more likely.

For all the iodides mentioned above, except t-butyl and ethylene

iodides, the overall reaction was given by the equation

$$2\ C_nH_{2n+1}I \longrightarrow C_nH_{2n} + C_nH_{2n+2} + I_2$$

In spite of this point of similarity, the rate equations and proposed mechanisms differed considerably. Thus, iso-propyl iodide gave first order kinetics,

$$\frac{-d\,[RI]}{dt} = k\,[RI]$$

Of the various mechanisms possible, that proposed by Schumacher[20] seems the most feasible,

i.e. $C_3H_7I \longrightarrow C_3H_7 + I$

$2C_3H_7 \longrightarrow C_3H_6 + C_3H_8$

$2I \longrightarrow I_2$

The rate-determining step should thus be the initiating unimolecular split, so that the activation energy should be identifiable with the carbon-iodine bond energy. Jones and Ogg[16] found this to be 42.9 k. cals. per mole, which is lower than expected from modern data.

Ethylene iodide[19,21] and sec-butyl iodide gave similar kinetics, both decompositions following the rate equation

$$\frac{-d\,[RI]}{dt} = k_1\,[RI] + k_2\,[RI]\,[I_2]^{\frac{1}{2}}$$

In each case, the first-order contribution to the rate was assumed to correspond to a direct unimolecular decomposition, while the second term was accounted for by a mechanism whose rate-determining step was a reaction of the type

$$I + RI \longrightarrow R + I_2.$$

The main iodine-producing reactions in the pyrolyses of n-propyl and iso-butyl iodides were found to be of this iodine-catalysed nature, the rate equation being

$$\frac{-d[RI]}{dt} = k[RI][I_2]^{\frac{1}{2}}$$

The iso-butyl iodide decomposition was investigated by Jones,[18] who accounted for the rate expression on the basis of a mechanism involving activated iodide molecules. This seems unlikely to be correct, in view of the history of other activated molecule mechanisms.

Jones and Ogg, in their paper on n-propyl iodide,[15] give a detailed discussion of possible kinetic schemes, and accept a somewhat complex mechanism involving isomerisation of the n-propyl radicals to the iso-propyl isomers, through reaction with iodine, i.e. $n\text{-}C_3H_7 + I_2 \longrightarrow iso\text{-}C_3H_7I + I$.

Schumacher[20] has criticised this mechanism, and suggests an alternative mechanism based, as before, on a reaction of the type

$$I + RI \longrightarrow R + I_2$$

An example of a radical attacking a parent iodide molecule, yielding an iodine atom and a radical dimer, is afforded by the pyrolysis of allyl iodide.[23] The proposed mechanism is

$$CH_2{=}CH.CH_2I \rightleftharpoons CH_2{=}CH.CH_2 + I$$

$$I + I \rightleftharpoons I_2$$

$$CH_2{=}CH.CH_2 + CH_2{=}CH.CH_2I \longrightarrow (CH_2 = CH.CH_2)_2 + I$$

The relative stability of the allyl radicals, due to resonance

"smearing" of the odd electron over the entire radical, is doubtless the main factor in permitting the iodide dissociation equilibrium to be established. Radicals not stabilised in this way are destroyed too rapidly by secondary reactions.

A somewhat similar situation is found in the case of benzyl iodide, the radical in this instance being the highly stabilised benzyl radical. The reaction has been investigated by Gow and Horrex,[3] and the mechanism found to be

$$C_6H_5CH_2I \rightleftharpoons C_6H_5CH_2 + I$$
$$I + C_6H_5CH_2I \rightleftharpoons C_6H_5CH_2 + I_2$$
$$I + I \rightleftharpoons I_2$$
$$2C_6H_5CH_2 \longrightarrow (C_6H_5CH_2)_2$$

The rate-determining step is the formation of dibenzyl.

Szwarc[23] had previously postulated the following mechanism for the decomposition:-

$$C_6H_5CH_2\,I \rightleftharpoons C_6H_5CH_2 + I$$
$$I + I \rightleftharpoons I_2$$
$$2C_6H_5.CH_2 \longrightarrow (C_6H_5.CH_2)_2$$

The rate-determing step is again the dimerisation of benzyl radicals, but the equilibrium was believed to involve only the unimolecular fission process and its reverse.

The method of radioactive tracers has been used by Noyes in thermal and photochemical studies of iodides in inert solvents, using radioactive iodine. For diiodoethylene,[24] allyl iodide,[25] benzyl

iodide[26] and sec-butyl iodide,[27] it was shown that iodine atoms were involved in the exchange between the iodide and the radioactive iodine. Also, for allyl and benzyl iodides, the reaction steps

$$R + I_2 \longrightarrow RI + I$$

$$I + RI \longrightarrow R + I_2$$

were shown to occur.

More direct proof of the occurrence of free radicals in the decomposition systems of organic iodides has been obtained by Lossing and his collaborators, by use of the mass spectrometer.[28,29] Thus methyl, allyl, and benzyl radicals were detected in the pyrolyses of the corresponding iodides, but the corresponding radicals did not appear in the cases of n-propyl and iso-propyl iodides. Methyl radicals were detected in these two cases, however, and these probably result from the decomposition of the expected propyl radicals.

The whole field of iodide decompositions has been critically reviewed by Steacie.[22] The general conclusion to be drawn from his assessment of the literature seems to be that, in most cases, the complexities of the reactions have not been fully explained.

A large number of iodides were pyrolysed by Butler, Mandel and Polanyi,[30,31] using a fast flow technique. Their work was intended only as a broad survey, to discover whether differences in bond strengths with varying molecular environments could be detected by the kinetic method. They used very short reaction times, thus

hoping to cut out the effects of secondary reactions. No attempt was made to establish the mechanism of the decompositions, the kinetics being assumed to be first order. Activation energies were calculated from their first order rate constants by assuming a value of $10^{15} secs^{-1}$ for the A- factor. In this way, for example, they estimated the carbon-iodine bond dissociation energy in methyl iodide to be 54 k. cals. per mole, a value in excellent agreement with modern data. The investigators themselves point out, however, that there are a number of puzzling complications in their results, and it seems unlikely that their work is reliable.

This flow system work was considerably extended in St. Andrews by Lapage and Horrex[32] and by Cundall and Horrex.[33] Using nitrogen as carrier gas, the overall reaction was shown to be

$$4\ CH_3I \longrightarrow 3\ CH_4 + C + 2\ I_2.$$

The primary step was concluded to be the unimolecular fission of the iodide molecule to give a methyl radical and an iodine atom. No chain reaction occurs, as the fastest rate observed was in the presence of toluene as radical acceptor.

At high total pressures, of the order 600 mms., in the presence of toluene, first-order constants could be derived from the results, given by $k_1 = 10^{15.7} . e^{-54,700/RT}$. The A- factor is in line with theoretical expectations, and the activation energy in good agreement with modern values for the carbon-iodine bond energy. Omission of the toluene in the above conditions gave first-order constants

$10^{7.55}.e^{-55,800/RT}$. This reduced rate was accounted for on the basis of considerable reverse reaction, the derived first-order constants not being sufficiently sensitive to detect the error in the assumed mechanism.

At low total pressures, in the absence of toluene, some surface effect was apparent, but the reaction was predominantly homogeneous. The rate was markedly dependent on the pressure of both iodide and nitrogen, and this was accounted for on the basis of the Lindemann theory of unimolecular reactions. Various carrier gases other than nitrogen were used, but their efficiencies in maintaining first-order behaviour differed markedly from data from other sources. There were other puzzling features, but these are more conveniently discussed later.

The behaviour of trifluoromethyl iodide on pyrolysis might be expected to be similar to that of methyl iodide, and this compound was investigated by Downs and Horrex.[2] A fast flow technique was initially used, the data being used to derive first-order constants, in a fashion similar to that used for methyl iodide by Cundall and Lapage. The general behaviour of the two substances was much the same, except that the CF_3 radicals, in the absence of a radical acceptor, were removed by dimerisation to give C_2F_6, whereas the methyl radicals produced methane plus elementary carbon, probably by a wall reaction. A fall-off in the first-order rate constants at low pressures was found for CF_3I, as for CH_3I, and the collision

efficiencies determined for various inert gases again disagreed widely with values obtained by other workers.

Eventually it was discovered that the reaction was more complicated than previously assumed, and that there were in fact two mechanisms operating under the conditions used. One was the unimolecular fission route, the other being the iodine catalysed decomposition of the type $I + RI \longrightarrow R + I_2$.

This type of behaviour is similar to that found by Gow and Horrex[5] for benzyl iodide, though in this latter case the relative stability of the benzyl radical enables a sufficient radical concentration to be built up for the reverse reaction rate to be maintained, and the equilibrium

$$I + RI \rightleftharpoons R + I_2$$

to be established.

A series of experiments in a static reaction system, using CF_3I with varying amounts of HI present, was then carried out. At the temperatures used, the contribution to the overall rate of the first-order process was negligible, the rate-determining step being $I + CF_3I \longrightarrow CF_3 + I_2$.

At high enough HI concentrations, the reaction became zero order with respect to HI. This was interpreted as being due to practically complete removal of the CF_3 radicals by the reaction

$$CF_3 + HI \longrightarrow CF_3H + I$$

At lower HI concentrations, the rate did depend on this parameter, and

this was suggested to be due to the back reaction

$$CF_3 + I_2 \longrightarrow CF_3I + I$$

competing successfully for the radicals. In a large excess of HI, this last reaction does not occur to any appreciable extent, as the chances of a radical colliding with an HI molecule are much greater than with an iodine molecule. Since both are exothermic, free radical reactions, almost every collision will be effective.

The reaction scheme proposed by Downs and Horrex for the CF_3I pyrolysis is:

$$CF_3I \longrightarrow CF_3 + I$$

$$I + CF_3I \longrightarrow CF_3 + I_2 \qquad (1)$$

$$CF_3 + I_2 \longrightarrow CF_3I + I \qquad (2)$$

$$CF_3 + HI \longrightarrow CF_3H + I \qquad (3)$$

$$I + I + M \rightleftharpoons I_2 + M$$

Ignoring the unimolecular contribution, and using a large excess of HI as a radical acceptor to cut out the back reaction (2), the rate equation deduced from this mechanism is

$$d\left[I_2\right]/dt = k_1.K^{\frac{1}{2}}.\left[CF_3I\right] \cdot \left[I_2\right]^{\frac{1}{2}},$$

where K is the iodine dissociation constant, and k_1 the rate constant for reaction (1) above.

The overall activation energy E should thus be related to E_1 by the expression

$$E = E_1 + \tfrac{1}{2}.\Delta H,$$

where H is the heat of dissociation of iodine. The value of E_1 determined in this way is related to $D(CF_3-I)$ by the equation

$$E_1-E_2 = D(CF_3-I) - D(I-I),$$

each side of the equation representing H for the process

$$I + CF_3I \rightleftharpoons CF_3 + I_2$$

Reaction (2) is known to have either zero, or very low, activation energy. If we assume E_2 to be zero, the value of $D(CF_3-I)$ deduced from the well-known value of D(I-I) and from Downs' value for E_1 turns out to be 51 k. cals. per mole. The fact that this is in excellent agreement with values obtained by independent methods is strong evidence in favour of the validity of the above mechanism for the CF_3I pyrolysis.

This work obviously has a bearing on the work of Ogg[1], who investigated the thermal reactions of methyl, ethyl, and n-propyl iodides with HI in a static reaction system. In the following discussion, methyl iodide will be referred to in particular, but it is probable that most of the remarks made will also be applicable to the others.

Ogg found that the reaction rate depended on the hydrogen iodide concentration, and interpreted his results on the basis of the scheme below.

$$CH_3I + HI \longrightarrow CH_4 + I_2 \qquad (4)$$

$$CH_3I \longrightarrow CH_3 + I$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (2a)$$

$$CH_3 + HI \longrightarrow CH_4 + I \qquad (3a)$$

$$I + I + M \rightleftharpoons I_2 + M$$

Two papers have recently been published,[54,55] criticising Ogg's interpretation of his data, and reinterpreting his results on the basis of a mechanism similar to that found for CF_3I by Downs.

$$I + RI \longrightarrow R + I_2 \qquad (1)$$

$$R + I_2 \longrightarrow RI + I \qquad (2)$$

$$R + HI \longrightarrow RH + I \qquad (3)$$

$$R + RI \longrightarrow R^1I + RH \qquad (5)$$

$$I + I + M \rightleftharpoons I_2 + M$$

A reaction scheme consisting of (1), (2), and (3), together with the iodine dissociation equilibrium, was suggested by Benson and O'Neal,[34] while Sullivan[35] also included (5).

Ogg accounted for the observed dependence of the rate on HI concentration by including the bimolecular reaction (4). This step is analogous to the four-centre reaction of hydrogen iodide alone. The range of concentration variables used by Ogg was limited, and in fact corresponds to the conditions in which Downs found the CF_3I reaction rate to be dependent on the pressure of HI. Arguing by analogy with the latter case, the rate should eventually become independent of the HI concentration above some limiting concentration. If the analogy is valid, and there is in fact a limiting value to the rate on increasing the HI pressure, then reaction (4) is ruled out.

It remains to provide an alternative explanation for the dependence of the rate on HI concentration, and this is readily done by assuming, as for CF_3I, that the HI acts as a radical acceptor. At low HI pressures, reaction (3) does not catch all the radicals, so that the back reaction (2) will play a significant role.

Other objections to Ogg's analysis can be pointed out. The value obtained for $D(CH_3-I)$ on this basis is 43 k. cals. per mole, which is almost certainly too low by about 12 k. cals. The A- factor found for the unimolecular fission of CH_3I was of the order 10^{12} secs.$^{-1}$, which is rather low for such a simple, bond-breaking process. The A- factor obtained for the bimolecular reaction (4) is of the order of 2×10^{11} litres moles^{-1} secs^{-1}, which is much higher than expected for a four-centre reaction. The analogous HI reaction has an A- factor smaller by a factor of ten. Transition state considerations,[54] even with the most favourable assumptions about the nature of the alkyl iodide-hydrogen iodide transition complex, do not give A- factors in excess of about 10^9 litres moles^{-1} secs^{-1}. The more complex case is expected to have a smaller A- factor, since rotational degrees of freedom in the non-reacting state are converted to vibrations in the transition state, the partition functions of the former exceeding those of the latter by a factor of the order of ten. Also, the activation energy deduced for reaction(4) is about 30 k. cals. per mole, which, since the activation energy for the analogous HI reaction is 44 k.cals. per mole, is certainly too low.

However, analysis of Ogg's data on the basis of the atomic reaction mechanism suggested by Benson and O'Neal[34] gives elementary rate parameters which are in reasonable agreement with thermochemical and other sources, and are in accord with theoretical considerations. Thus, for example, Benson and O'Neal found that an upper limit for E_1, in the case of methyl iodide, was 20.5 k. cals. per mole, on the assumption that A_1 could not exceed 2×10^{11} litres $moles^{-1}$ $secs^{-1}$. They also found that, for the specific temperature 280°C, $k_3/k_2 = 0.15$, and by estimating values for various entropy changes, found log A_3 to be 9.47 litres $moles^{-1} secs^{-1}$. These are all reasonable values in the light of modern ideas on Arrhenius parameters. The value of E_1 leads to an upper limit for $D(CH_3\text{-}I)$, which is in good agreement with thermochemical data.

It is relevant here to consider some recent work on the hydrogen iodide equilibrium,

$$2\,HI \rightleftharpoons H_2 + I_2.$$

In particular, the forward process is analogous to the reaction of an alkyl iodide with HI, and has long been regarded as the classic example of a bimolecular, four-centre reaction. It has now been shown to proceed also by a simultaneous atomic route. Thus, Benson and Srinivasan[56] critically discussed Bodenstein's[39] data for the HI reaction, pointing out various discrepancies in its interpretation as a purely bimolecular process. For example Bodenstein's bimolecular activation energy has an abnormally high

temperature coefficient of 21 cals moles^{-1} degrees^{-1}. This value was shown to be compatible with a mechanism involving simultaneous bimolecular and atomic chain processes, the latter making a significant contribution to the overall rate above 600°K.

Experimental evidence in favour of this suggestion was found by Sullivan,[37] who accounted for his results on the basis of the reaction scheme shown.

$$I_2 + M \rightleftharpoons 2I + M$$

$$2HI \rightleftharpoons H_2 + I_2$$

$$I + H_2 \longrightarrow HI + H$$

$$H + HI \longrightarrow H_2 + I$$

$$H + I_2 \longrightarrow HI + I$$

$$I + HI \longrightarrow H + I_2$$

The occurrence of the reaction step

$$I + HI \longrightarrow H + I_2,$$

which is analogous to the step

$$I + RI \longrightarrow R + I_2$$

found by Downs[2] for CF_3I, and by Gow[5] for benzyl iodide, strongly suggests that such an iodine atom catalysed reaction will also occur in the pyrolysis of other iodides, and of methyl iodide in particular. Sullivan showed that, in the case of HI, the atomic mechanism accounted for 10% of the overall reaction at 653°K, and for 27% at 738°K, when the iodine pressure is half an atmosphere.

Sullivan found the reaction to be completely homogeneous in

pyrex reaction vessels. There is, however, a great deal of conflicting evidence[37,38,39,40] on the question of a possible heterogeneous contribution to the reaction.

There would thus appear to be little doubt that the mechanism proposed by Ogg for the thermal reaction of methyl iodide with HI is untenable. In the light of the evidence discussed above, it seems likely that a mechanism of the type suggested by Benson and O'Neal[34] and Sullivan[35] is operative. If this is in fact the case, it would explain certain puzzling features observed by Lapage[41] in her fast-flow studies of the methyl iodide pyrolysis. A study of the variation of percentage decomposition with reaction time showed that there was an approximately linear relationship between the two at low percentages of reaction. However, the linear plots did not extrapolate to the origin, but showed definite intercepts on the time axis. This is explained most simply by considering that the gas takes this length of time to heat up from room temperature on entering the furnace. However, it was found that the times required for different furnace temperatures did not follow any logical pattern, lower temperatures requiring longer heating times.

If, however, the reaction is regarded as being mainly auto-catalytic in nature, as suggested, then smooth curves typical of this type of behaviour can be drawn through the origin and the experimentally determined points.

Ogg remarks in his paper[1] that the first 10% of reaction was

"abnormally slow", this effect being enhanced by large amounts of HI. He accounted for this by postulating anomalously slow mixing of the reactants, but it seems much more likely that this period corresponds to an induction period, during which the concentration of a catalytic agent is being built up. The reaction time - percentage decomposition curves found by Lapage can be similarly interpreted.

BOND ENERGIES : INTRODUCTION.

There are two definitions of the concept of bond energy which are widely used, and which are not equivalent. Thus, early tables of bond energies[42] consisted of values of "bond energy terms", defined as quantities which may be assigned so that their sum for any one molecule gives its heat of formation from the separated atoms. Emphasis is thus laid more on the approximate constancy of the values for any one bond, rather than on differences from the average. However, it is well known that the reactivity of a bond varies with its molecular environment, and since chemical change involves the making and breaking of bonds, it seems reasonable to assume that these differences in the reactivity of any one link are related to variations in the strength of the bond.

From this point of view, a more useful concept is the "bond dissociation energy", defined as the energy absorbed when a gaseous compound is decomposed, by the breaking of the bond, into two unexcited radicals or atoms.

An excellent monograph by Cottrell[43] has been published, reviewing the theoretical and practical aspects of the determination of both quantities, and critically summarising values obtained at the date of publication. The present work was aimed at obtaining a value of the carbon-iodine bond dissociation energy in methyl iodide,

and the following notes will refer briefly to previous determinations of this quantity only.

PREVIOUS DETERMINATIONS OF $D(CH_3-I)$.

The most recent determination of this quantity was by Carson, Carter and Pedley,[44] who found the heat of reduction of methyl iodide by an ethereal solution of lithium aluminium hydride in an adiabatic calorimetric system. A value of 5.8 k. cals. per mole for $\Delta H^\circ f$ of CH_3Ig at 25°C was obtained, which was used to obtain a value of $D(CH_3-I)$ from the relation

$$D(CH_3-I) = \Delta H^\circ f(CH_3) + \Delta H^\circ f(I) - \Delta H^\circ f(CH_3Ig).$$

The value of $\Delta H^\circ f(CH_3)$ was taken as 52.0 k.cals. per mole, based on $D(CH_3-H)$ = 101.9 k.cals. per mole,[55] and on $\Delta H^\circ f(CH_4.g)$ = -17.889 k.cals. per mole and $\Delta H^\circ f(H)$ = 52.089 k. cals per mole. These heats of formation, together with $\Delta H^\circ f(I)$ = 25.48 k. cals. per mole, are well established. (National Bureau of Standards, 1952). The bond dissociation energy so derived for room temperature, $D(CH_3-I)$, is thus 55.7 k. cals. per mole.

The authors also give a summary of previously determined values of $D(CH_3-I)$. These are listed in Table I, some of the values quoted being different from those originally given by the authors, due to changes in accepted values for various subsidiary thermal data and bond dissociation energies.

TABLE I

Values of $D(CH_3-I)$ quoted by Carson, Carter and Pedley.[44]

Method	$D(CH_3-I)$, k.cals. per mole	Original Reference.
Thermochemical	55.7	44
"	55.7	45
"	54.3	46
"	52.5	47
"	53.0	48
"	54.3	49
"	55.0	50
Electron Impact	50.7	51
"	53.4	52
"	53.4	53
"	53.7	54
Kinetic	54	51

A value of 53-54 k. cals. per mole thus appears to be well established. The only kinetic determination quoted is that of Butler and Polanyi, which, as the authors point out, involves several discrepancies, the agreement with other data probably being fortuitous. The only other estimate quoted in the literature as being obtained by a kinetic method is that of Ogg,[1] which was discussed at length in a previous section.

There are two other general methods which have been applied to the determination of bond dissociation energies. These are the equilibrium method and the spectroscopic method, the former not being

applicable to the case of organic iodides, due to the high reactivity of the dissociation fragments.

Iredale[54] found that methyl iodide displayed a continuous spectrum, the long wave-length limit being 3950 Å in the liquid phase, and 3500 Å in the vapour phase. However, Porret and Goodeve[55] found that, for the vapour, the continuum limit depended on both the iodide pressure and on the length of the absorption tube, thus making impossible any accurate determination of the dissociation energy from the spectrum.

Iredale[56] obtained a value of 52 k. cals. per mole from his treatment of the Raman spectra data of Dadieu and Kohlrausch.[57] He supported this value by considering that the CH_3 radical can be regarded as similar to the fluorine atom, and extrapolating from the following data:-

Bond.	I - I	I - Br	I - Cl	I - CH_3
D(k.cals.per mole)	36	46	50	(52?)

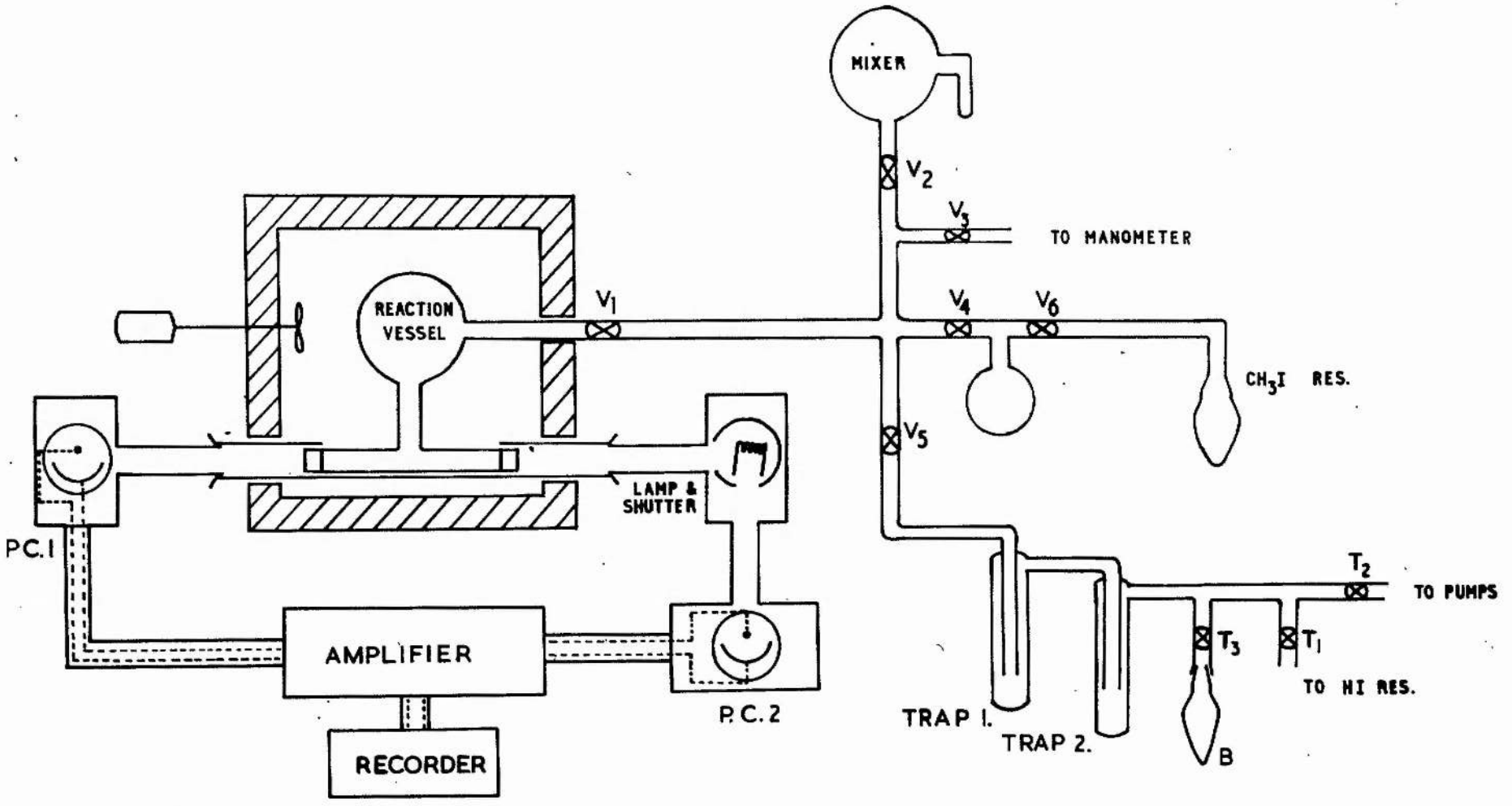

MIXER
V2
V3
TO MANOMETER
REACTION VESSEL
V1
V4
V6
CH3I RES.
V5
LAMP & SHUTTER
PC.1
T2
TO PUMPS
AMPLIFIER
T3
T1
TO HI RES.
P.C.2
TRAP 1.
TRAP 2.
B
RECORDER

FIG. 1

THE PRESENT INVESTIGATION.

The foregoing criticism of Ogg's paper[1] on the thermal reaction between methyl iodide and HI refers only to his interpretation of his data, and not to the experimental results themselves. The data obtained by Ogg were in fact so extensive that, apart from one completely reported run for each of the three iodides investigated, he was forced to resort to publishing his results in a condensed form. This made the task of the two sets of workers,[54,55] who reinterpreted his results, much more difficult, with a corresponding lack of precision in their quantitative conclusions.

Ogg followed the progress of the reaction by photometric estimation of the iodine produced, a method which lends itself to practically continuous observation of the reaction system. It was decided to use a similar method in the present work, taking advantage of the improvements in equipment available since the time of Ogg's investigation.

APPARATUS AND EXPERIMENTAL TECHNIQUE.

A diagram of the apparatus in shown in Fig. 1. It consists essentially of three systems:

(1) A conventional glass vacuum system.

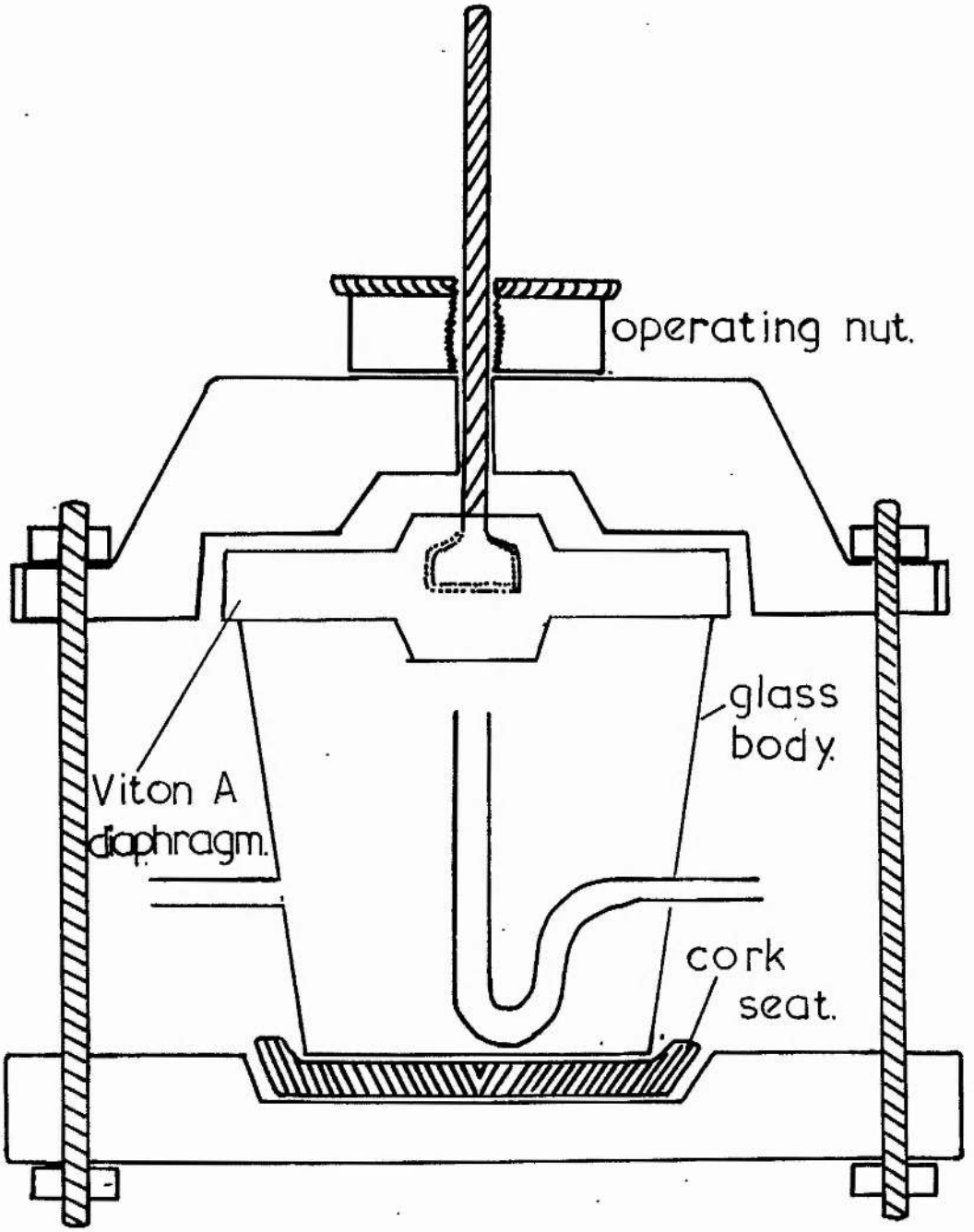


FIG. 2

(2) An electronically controlled furnace, with a high-speed fan to ensure uniformity of temperature.

(3) A photometer for the estimation of the iodine produced.

Evacuation of the system.

A mercury diffusion pump of conventional design was used, backed off by an Edwards "Speedivac" rotary oil pump. A trap cooled in liquid air froze out condensible substances. Pressures, measured on a McLeod Gauge, could be obtained lower than 10^{-5} mms. of mercury.

Taps and Valves.

The usual ground-glass taps were used where possible in the vacuum system. However, since methyl iodide, HI, and iodine all either react with or dissolve in tap-grease to some extent, this could not be used in parts of the system which were to be in contact with the reaction mixtures.

Glass-bodied valves with rubber diaphragms offered a solution to the problem, but unfortunately most materials normally used for diaphragms are embrittled by the chemical mixtures to be employed in this work. Valves with diaphragms made of "Viton A", an inert fluorinated rubber, were available from Springhams and Co., and these were tried. The diaphragms were found to be resistant to the chemicals used, but unfortunately the valves were not vacuum tight, and had to be considerably modified. A diagram of a modified valve is shown in Fig. 2.

Reaction Vessel and Premixer Bulb.

The reaction vessel consisted of a two-litre pyrex bulb, to which was attached an optical cell, 15 centimetres long, with evacuated end-sections to cut down heat losses. This optical cell rested lengthwise in a piece of inconel tubing, partially cut away to form a trough, which formed part of the mechanical framework for the optical train of the photometer.

The reaction vessel dead-space was kept as small as possible by having the valve V_1 as close as possible to the furnace exit. This valve was heated electrically, to prevent any possibility of iodine condensing on its walls during the course of a run.

The premixer bulb, which was used to premix the reaction gases before each run, was also a two-litre pyrex bulb, which could be warmed to about 40°C. This bulb had a small sidearm which could be cooled in liquid air, and thus be used to freeze reactants into the bulb from the injection systems.

Hydrogen Iodide Reservoir.

The HI was stored in a series of pyrex bulbs of total volume 16 litres, painted black to prevent decomposition of the HI by light. The reservoir was shut off by a ground-glass tap lubricated with silicone grease.

The Furnace and Temperature Measurement.

The furnace consisted essentially of a large firebrick box, of internal dimensions 18" x 12" x 12". The walls were 5" thick, and the

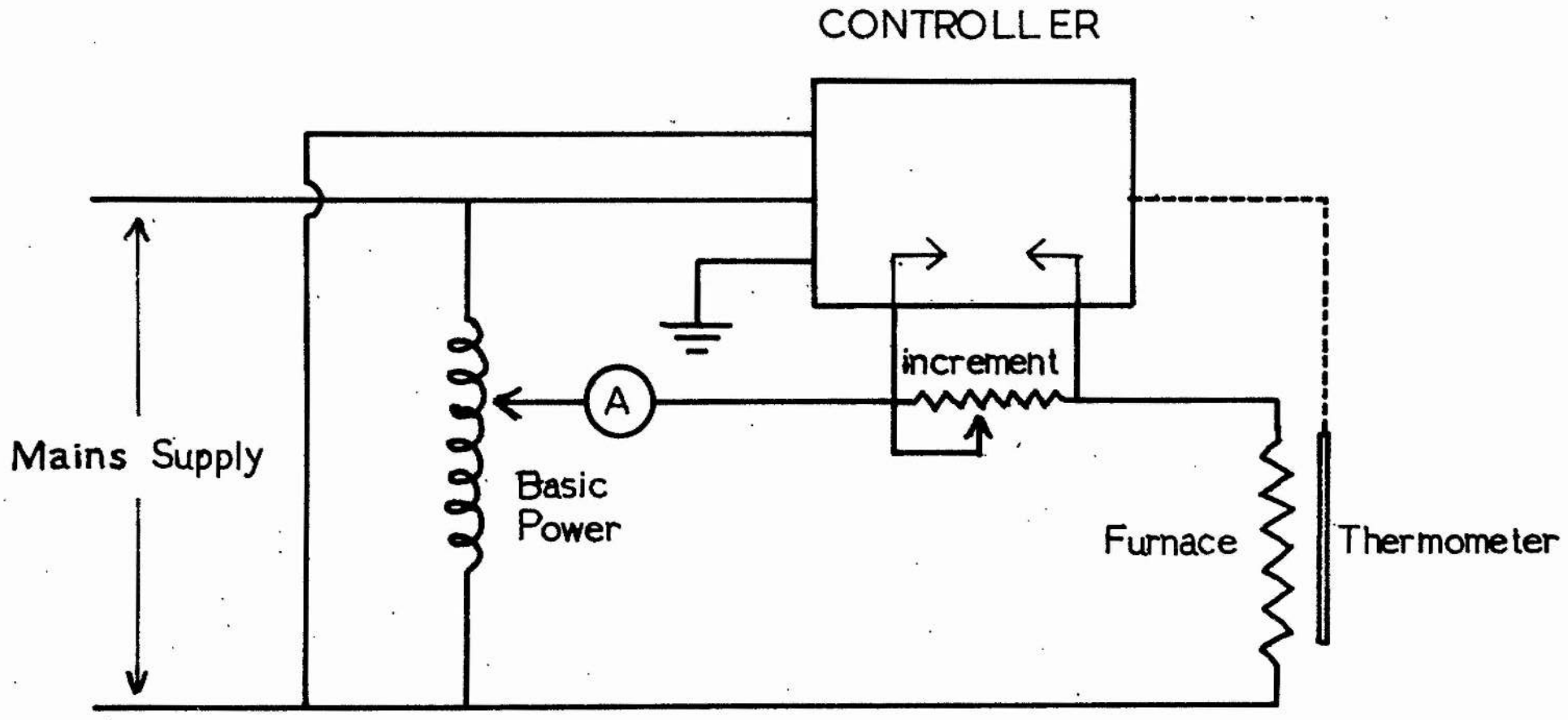

CONTROLLER
increment
A
Mains Supply
Basic
Power
Furnace
Thermometer

FIG. 3

whole structure was enclosed in a sheet-metal case. One of the sides was detachable in two halves, these acting as doors allowing access to the interior.

The heating was provided by a series of Bray strip heaters mounted on an iron framework, with a sheet-steel radiation shield between the heaters and the reaction vessel. The temperature was controlled electronically, the sensing element being a platinum resistance thermometer. The controller operated by switching in and out an increment resistance in series with the furnace windings, the percentage of the time for which the increment was shorted out, and a higher current thus flowing through the furnace heaters, being determined by the actual temperature of the furnace as sensed by the resistance thermometer. A diagram of the arrangement is shown in Fig.5.

This furnace was rather large, its size being dictated by the fact that the reaction vessel had to be large enough to contain amounts of iodine which could be accurately estimated by titration, for the calibration and subsequent checking of the photometer.

The size of the furnace made temperature uniformity something of a problem, and some difficulty was experienced with this matter. An inconel fan, 7.5 inches in diameter, driven at high speed by an electric motor, effectively circulated the air inside the furnace. The main trouble was due to vibrations from the fan being transmitted to the photometer, but suitable rigid, independent mounting overcame

this trouble.

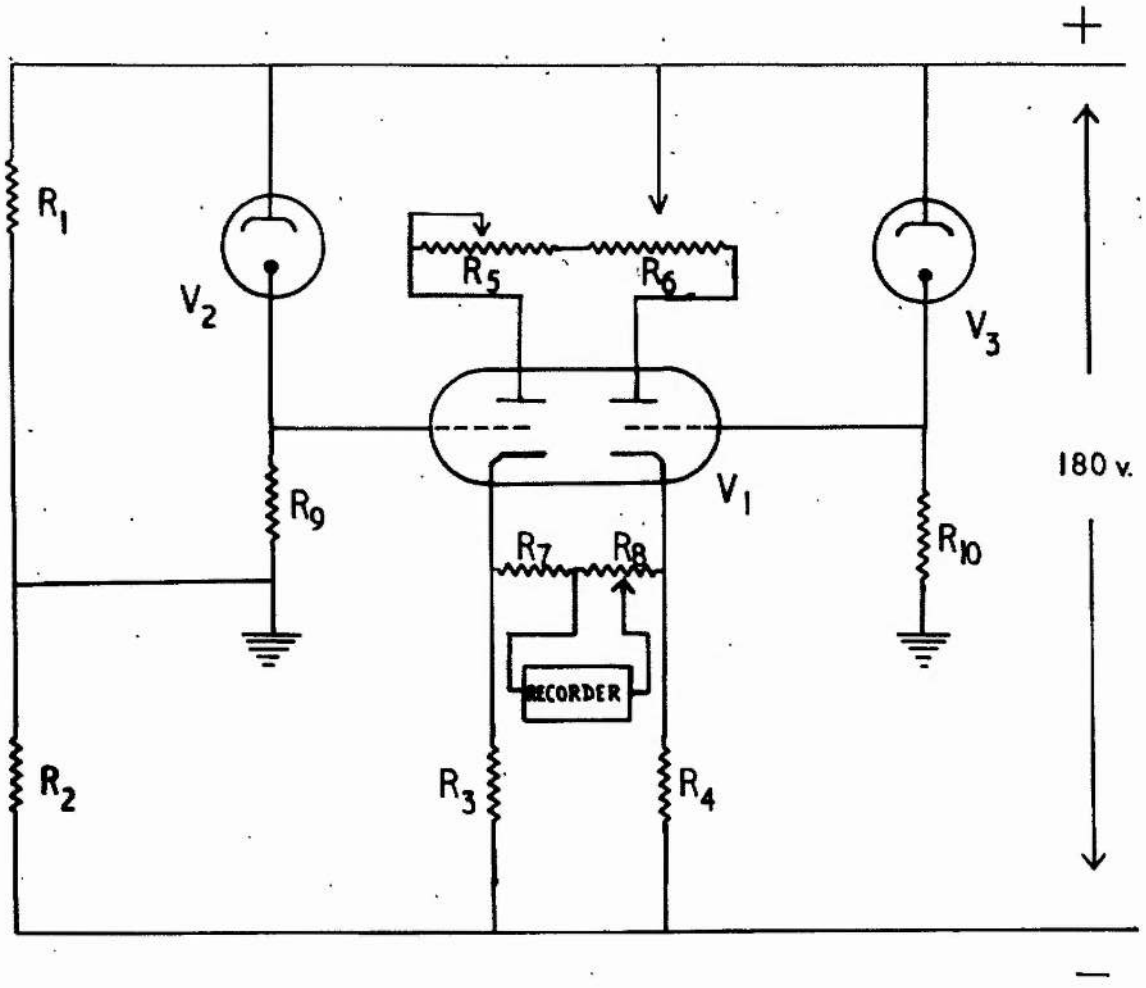
The position inside the furnace of the heaters, and the power developed in each, was found to affect the temperature distribution at lower fan speeds. When these were adjusted to the optimum conditions, and the fan speed increased, the largest temperature difference that could be detected, using copper-constantan thermocouples, was 2°C. This was the temperature difference between two corners of the furnace diametrically opposed to one another. In the body of the furnace, with the thermocouple junctions placed in various positions on the surface of the reaction vessel, a maximum temperature difference of 1°C could be detected. In practice, the temperature was measured by a chromel-P-alumel thermocouple, using the calibration of Roeser, Dahl and Gowens.[58]

The optical cell was covered by a sheath of nickel foil to prevent dust from being blown on to the optical surface when the fan was operating.

All gaps in the furnace wall, surrounding the thermocouple, resistance thermometer, reaction vessel exit, and the brass tubing constituting the optical train of the photometer, were packed with glass wool.

The Photometer.

The optical train was mounted on a rigid optical bench, consisting of four $\frac{3}{4}$" steel bars, bolted at each end to a $\frac{3}{8}$" steel plate. A



$R_1 = 540\ k\Omega$

$R_2 = 150\ k\Omega$

$R_3 = R_4 = 240\ k\Omega$

$R_5 = 50\ k\Omega$

$R_6 = 100\ k\Omega$

$R_7 = 10\ k\Omega$

$R_8 = 2{\cdot}5\ k\Omega$

$R_9 = R_{10} = 37\ M\Omega$

$V_1 = 6SL7$

$V_2 = V_3 =$ G.E.C. photocell BMV 31

FIG. 4

length of 1" x $\frac{1}{8}$" angle-iron was bolted to the bottom of each plate, perpendicular to the steel bars, and this in turn rested on a sponge-rubber seating attached to the table on which the whole apparatus was built. The object was to obtain a rigid, stable structure, which would not be affected by any vibrations or other disturbances arising from other parts of the apparatus.

On the optical bench were mounted two adjustable stands, from which were supported the photocells, lamp-housing, and the optical train. This latter consisted of telescopic brass tubing, which rested in V-shaped supports projecting from the stands. The main optical path, that to photocell 1, also contained the glass optical cell resting in its inconel trough in the furnace.

The photocells, which were G.E.C. Type BMV 31, were housed in brass cases supported by clamps from the adjustable stands. The cases were earthed, and connections soldered to the pins of the photocell valve bases were enclosed in earthed metal cans, as they were found to be extremely susceptible to electrostatic effects. All photometer wiring exterior to the amplifier cabinet was made with rigidly fixed screened cable. These leads seemed to be very sensitive to stray electrical effects.

The amplifier design was based on that used by Anderson, Scheraga and Van Artsdalen,[59] the circuit diagram being shown in Fig. 4. It is essentially a balanced cathode-follower circuit, and was built in an air-tight cabinet provided with dessicant, this cabinet also housing

the H.T. batteries. The valve filament current was supplied by accumulators.

The light source was a 12 volt 56 watt car headlamp bulb, which was run on A.C. mains via a constant voltage transformer and a step-down transformer. A rheostat was also in series with the lamp, so that the light intensity could be varied at will. A shutter was arranged so that either one, or both, or neither, of the photocells could be illuminated. The beam to each photocell came from the lamp through a system of pinholes, stops and lenses, mounted in a length of telescopic tubing, to give as nearly as possible parallel beams. An Ilford Spectrum Filter No. 605 was also interposed in each beam, to give a wavelength range of 4,700 - 5,200 Å. At 600°K, the ε-value for iodine in this region is conveniently about 500, and the photocell response is also satisfactory in this spectral range. There is no absorption by any of the other reaction components in this region.

One beam passed through the optical cell portion of the reaction vessel, falling on photocell 1. Light-baffles were screwed to the furnace wall at the points of entry of the optical train into the furnace. The other beam, at right-angles to the first, fell on photocell 2. This optical path was fitted with an iris diaphragm, so that the amount of light falling on photocell 2 could be adjusted independently of that falling on photocell 1.

The signals from the two photocells controlled the grids of the 6 SL 7 double-triode valve. Any difference in potential existing

between the two cathodes of the 6 SL 7 gave rise to a flow of current through R_7 and R_8, and hence to a reading on the strip-chart recorder.

In practice, with neither photocell illuminated, the recorder was set to some convenient reading by means of the balancing potentiometers R_5 and R_6. With the reaction vessel pumped clean, the shutter was then rotated so that both photocells were illuminated, and the recorder reset to its previous position by adjustment of the iris diaphragm. This meant that the amount of light falling on the two photocells was the same, or strictly speaking, corrected so that the two grid potentials were the same, differences in the photocell sensitivities and in the grid-leak resistances being accounted for. The shutter was then rotated so that only photocell 2 was illuminated, and the full-scale deflection of the recorder adjusted by means of R_8.

In effect, this means that the recorder deflection when photocell 2 only is illuminated is a measure of I_o, the light incident on the iodine in the reaction vessel. Illumination of photocell 1 only gives a measure of $I_{transmitted}$, and when both are illuminated, the difference signal fed to the recorder is a measure of $I_o - I_{transmitted}$, i.e. of $I_{absorbed}$. It is better practice to measure $I_{absorbed}$, since small amounts of iodine will give small values of this quantity, which can be measured directly as the difference signal. If $I_{transmitted}$ were followed, small amounts of iodine in the optical cell would only give rise to small variations in a relatively large recorder reading, with a resulting loss of precision.

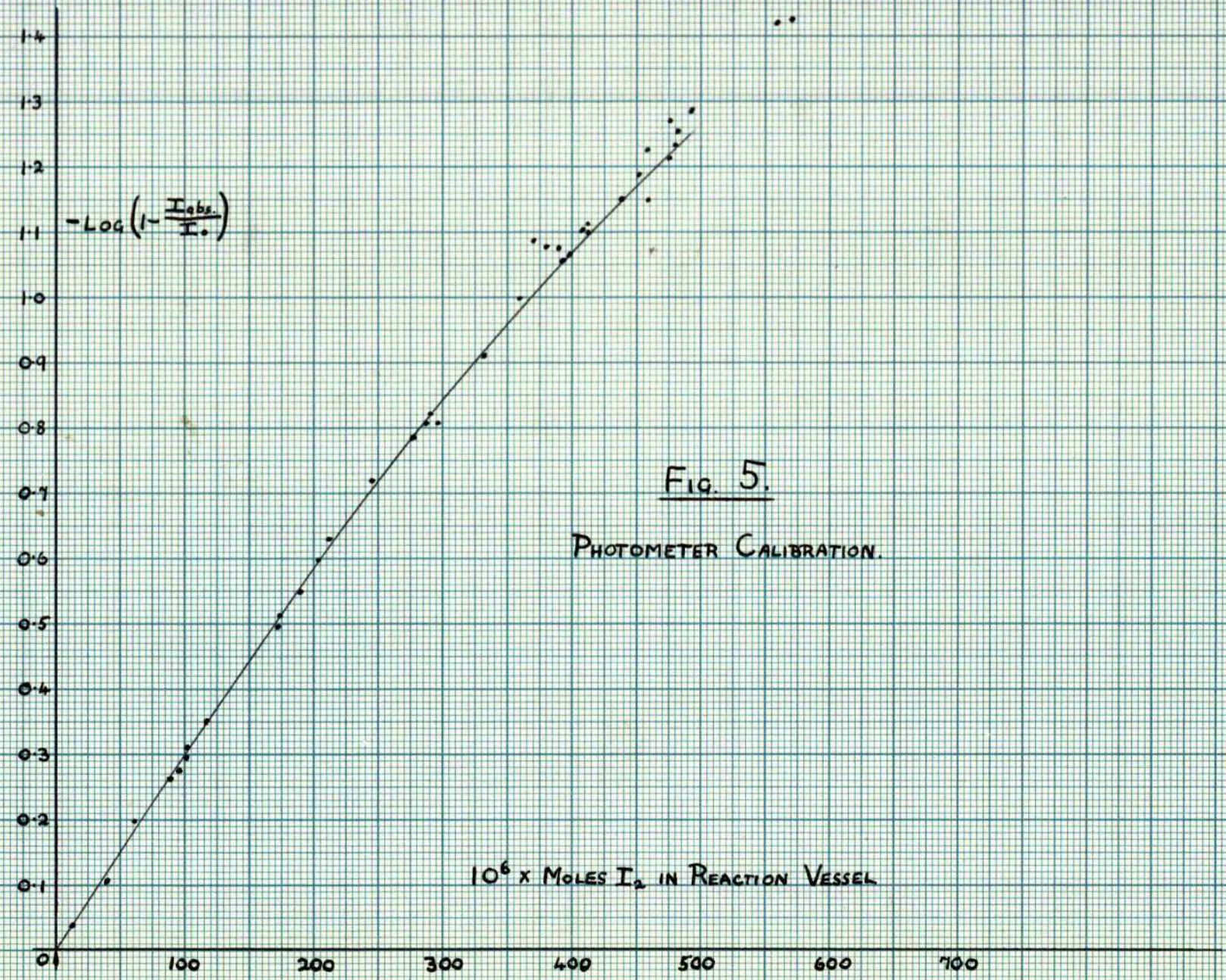


Fig. 5.

Photometer Calibration.

The theoretical relationship between the light intensities and the concentration of the absorbing substance is given by Beer's Law:

$$\log\left(1-\left(I_{absorbed}/I_{o}\right)\right) = -\varepsilon.c.d.,$$

where d is the path length and c the concentration of the absorbing medium. For constant d and constant volume of the reaction vessel, a linear relation should be observed between the logarithmic Beer's Law function and the number of moles of iodine in the reaction vessel. The calibration curve obtained for the present system is shown in Fig. 5.

The range of the photometer lies in the region 0 to 500 x 10^{-6} moles of iodine in the reaction vessel. Since the latter has a volume of 2.40 litres, (see Appendix II), this corresponds to a concentration range of about 0 to 200 x 10^{-6} moles per litre. At the lower, more sensitive end of the concentration scale, differences of 0.5 x 10^{-6} moles of iodine in the reaction vessel could be detected. At lower concentrations, the calibration curve approximates closely to a straight line, but at higher concentrations shows a definite curvature. This is doubtless due to the fact that the radiation used was not strictly monochromatic.

The calibration was obtained under conditions as similar as possible to reaction conditions. Thus, a mixture of a large excess of HI plus a little air was admitted to the hot reaction vessel. The oxygen oxidised some of the HI to iodine, the recorder readings corresponding to I_o and $I_{absorbed}$ were noted, and the mixture was then

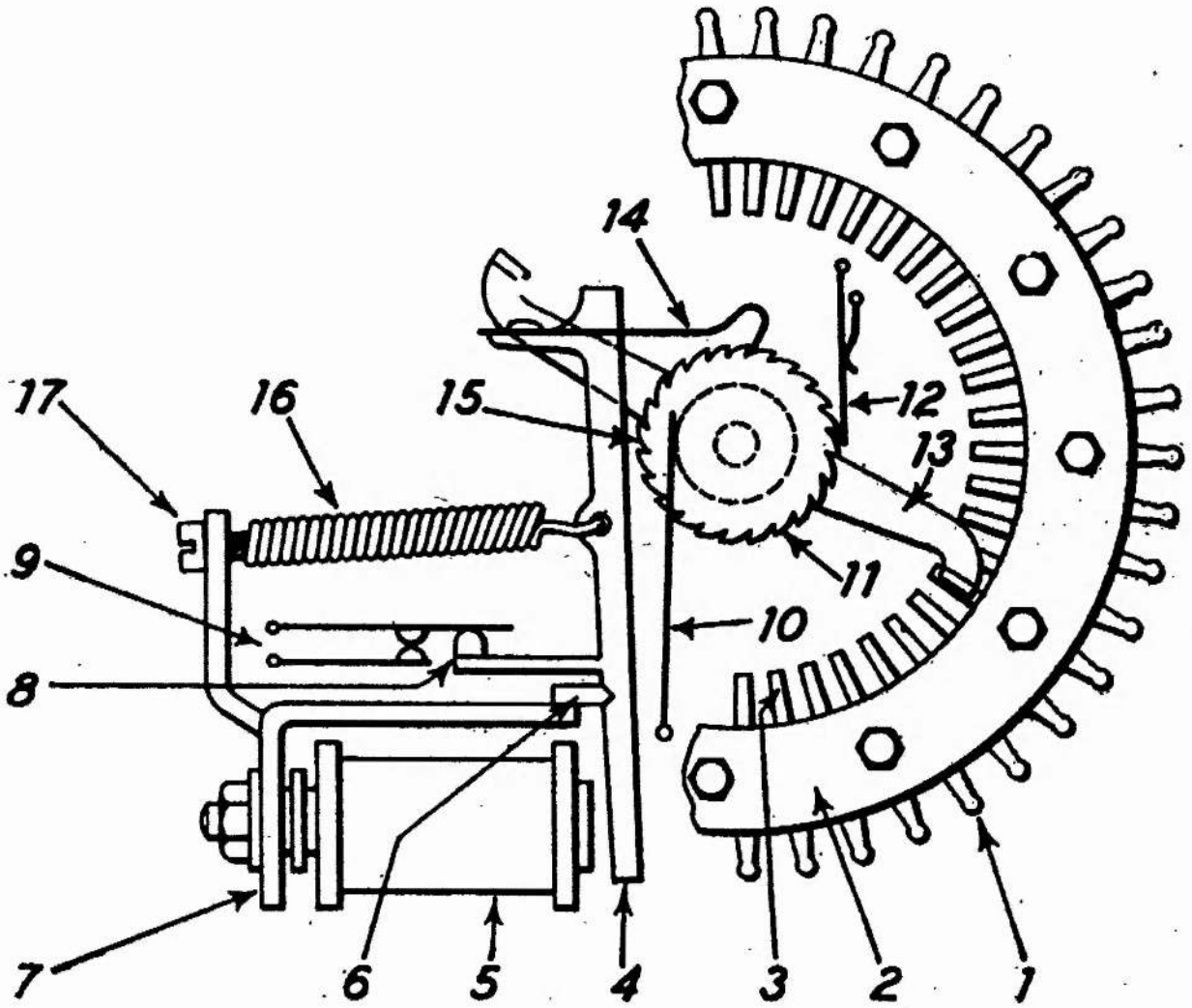


Fig. 6 —UNISELECTOR SWITCH

1. Soldering lugs
2. Bracket
3. Stationary contacts
4. Armature
5. Electromagnet
6. Knife edge
7. Yoke of relay coil
8. Ebonite collet
9. Contacts
11. Toothed wheel
12. Retaining pawl
13. Wiper
14. Gathering pawl
16. Adjustable spring
17. Adjusting screw

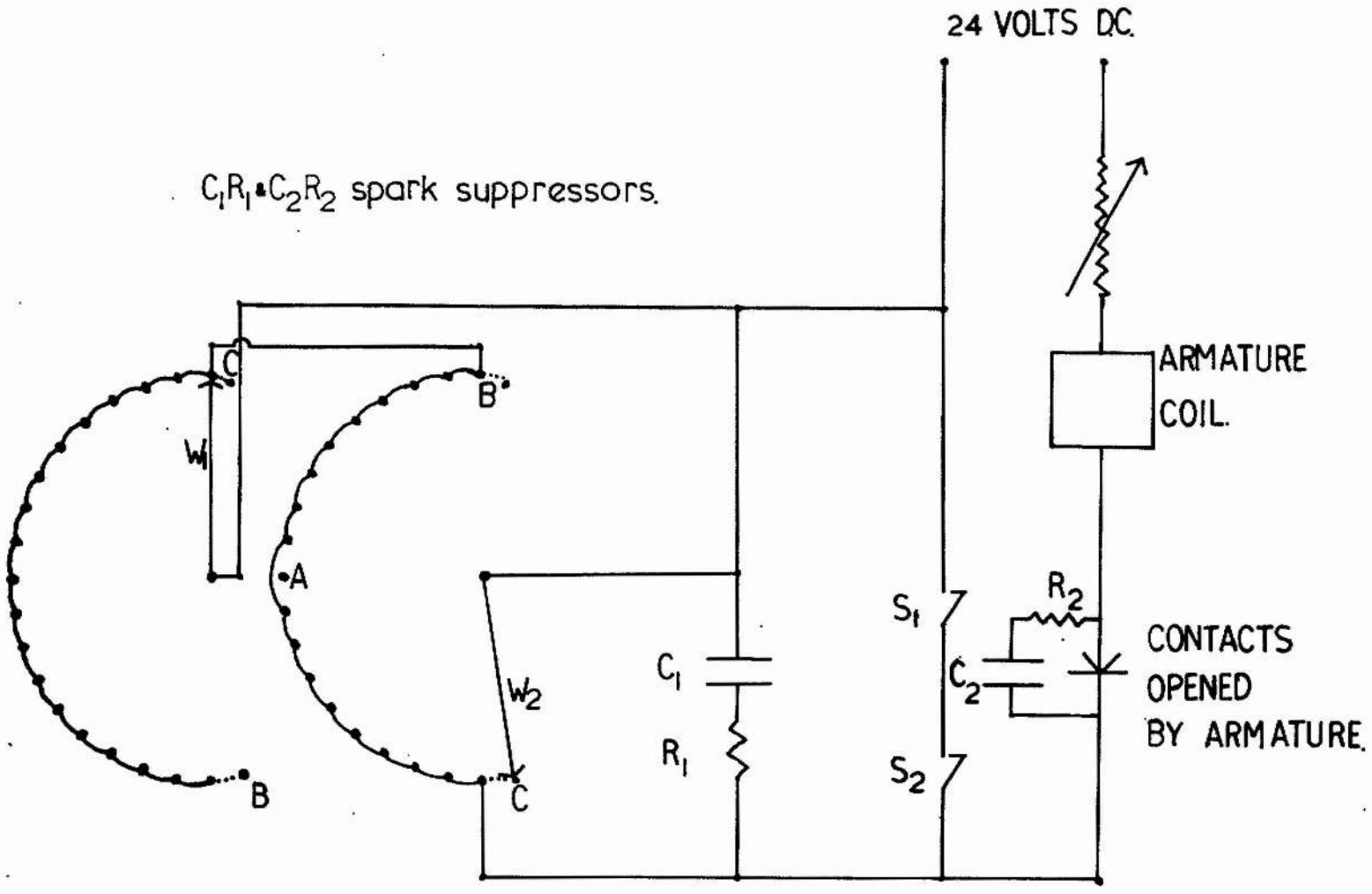

24 VOLTS DC.
C_1R_1 & C_2R_2 spark suppressors.
C
B
W1
A
W2
B
C
C_1
R_1
S_1
S_2
R_2
C_2
ARMATURE
COIL.
CONTACTS
OPENED
BY ARMATURE.

FIG. 7

frozen down into trap 2, cooled in liquid air. After pumping out, V_5, T_1 and T_2 were closed, T_3 was opened, and a cardice-acetone bath was put round trap 2, with a liquid air bath round the small bulb B attached to T_3. The HI distilled from the trap to the bulb, leaving the iodine in the trap, which could then be removed, and the iodine titrated with standard thiosulphate.

Having obtained a calibration, a measurement of iodine concentration involved a measurement of the two quantities I_o and $I_{absorbed}$. This means that, for each measurement, the shutter must be swung so that both photocells are illuminated, time allowed for the recorder to attain its equilibrium position, the shutter then swung so as to illuminate photocell 2 only, sufficient time allowed again, and the shutter finally swung so that neither photocell is illuminated. The recorder now follows any drifts in the photometer zero, caused by variations in photocell dark current, or by other effects.

The mechanism chosen to perform this cycle of operations was a telephone uniselector switch. This is effectively a self-actuating motor, and is shown diagrammatically in Fig. 6. A detailed description of the mode of operation has been given by Walker.[60] The arrangement used for the present purpose is shown in Fig. 7. The banks of contacts were wired so that there were three "dead" positions, A,B and C, at which the contact wipers came to rest. A flexible drive was taken from the central spindle on which the

contact wipers W_1 and W_2 are mounted at 180° to one another, and this was connected to the shutter. Since the cycle of operations B ⟶ C ⟶ A ⟶ B involves angular movements of 180°, 90° and 90°, respectively, the shutter will perform the corresponding rotations, which are those required for the cycle (neither photocell illuminated) ⟶ (both illuminated) ⟶ (photocell 2 only illuminated) ⟶ (neither illuminated), if position B on the uniselector is made to correspond to the shutter setting such that both photocells are blacked out. The cycle of readings obtained on the recorder corresponding to the above is (photometer zero) ⟶ ($I_{absorbed}$) ⟶ (I_o) ⟶ (zero reading).

A mechanism was required which would move the uniselector off the "dead" positions after a suitable time. This was provided by the microswitches S_1 and S_2, which, when closed simultaneously for a short time, pulsed the armature coil, whereafter the mechanism was self-actuating until the next "dead" position was reached. S_1 and S_2 were operated by cams driven from the same electric motor via suitable gearing arrangements. This arrangement made possible the automatic recording of iodine concentration as often as once every 35 seconds, if required.

Purification of materials.

Methyl iodide: this was a B.D.H. product. It was purified by distillation, the fraction boiling in the range 42.3 - 42.6°C being retained and stored in a dark, glass-stoppered bottle, over dessicant

and mercury. It was found that it remained clear and colourless after 18 months when kept in this way.

Hydrogen iodide: this was prepared by dropping a 55% solution (ex Albright and Wilson) on to phosphorus pentoxide, under a water-pump vacuum. The gaseous HI was frozen out into a trap cooled in liquid air, whence it could be transferred to the HI reservoir. It was purified by distillation from cardice-acetone to liquid air.

Description of an Experiment.

It was the usual practice to inject the reaction mixture into the premixer bulb in the evening, so that the gases could mix thoroughly overnight, and to perform the experiment the next day.

Injection of the HI to the mixer was done using the following procedure. After evacuation, all taps and valves were closed except V_2, V_3 and V_5. HI was then admitted through T_1, until the desired pressure was reached as read on the manometer. T_1 was then closed, and liquid air put round trap 2, freezing down the HI. After pumping for a few minutes through T_2, V_3 and T_2 were closed, cardice-acetone baths were put round traps 1 and 2, liquid air round the premixer side-arm, and the HI distilled from Trap 2 to the side-arm, impurities, consisting of water and iodine, being retained in the traps.

Methyl iodide was injected by allowing the standard volume between V_4 and V_6, at a measured temperature, to be filled with a known vapour pressure of the iodide. The standard volume of 155 ccs. was surrounded by a water bath, which acted as a thermal buffer whose

temperature could readily be measured to within 0.5°C or better. The methyl iodide reservoir was maintained at 0°C by means of ice and water, and the standard volume was filled with the vapour through V_6, with V_4 closed, the vapour pressure at 0°C being taken as 141 mms.[61] After equilibration, for which 30 minutes were usually allowed, V_1, V_3, V_5 and V_6 were closed, and V_2 and V_4 opened, so that the iodide vapour could enter the premixer bulb and be frozen down in the side-arm. The moles of methyl iodide injected were calculated from the ideal gas law.

When both reactants had been frozen down into the premixer, V_2 was closed, the liquid air removed from around the side-arm, and the reactants allowed to vapourise and mix thoroughly.

It was found that reproducible behaviour could only be obtained if the reaction vessel was left overnight with HI in it. This must have had some kind of seasoning effect on the walls of the reaction vessel, and is discussed more fully in a later section.

At the start of a run, the HI was pumped out of the reaction vessel, with liquid air round the traps, and the photometer balanced as described previously. The furnace temperature was checked over a period of about 20 minutes, to ensure that furnace conditions had settled down properly. (The furnace circuit and fan were controlled by a time-switch, which could be preset as desired).

V_3, V_4 and V_5 were closed, V_1 left open, and the run started by opening V_2. The recorder chart motor was started, as was the

motor driving the cams which pulsed the shutter mechanism. V_1 was then closed off, and the progress of the reaction was followed automatically, iodine concentrations being measured as described above, and the time being read off the time-scale on the recorder chart.

The portion of the reaction mixture which did not equilibrate into the reaction vessel was analysed for HI. This was done by freezing down into the bulb B, which had previously been filled with outgassed distilled water. The bulb and its contents were allowed to warm up, when the HI dissolved in the water, and after freezing down in liquid air again, air was admitted to the bulb, which could be removed from the system, and its contents analysed for HI by acid-base titration.

When the reaction had proceeded to the required extent, T_2, T_5, V_2, V_3 and V_4 were closed, liquid air was put round trap 2, and the reaction mixture frozen down via V_1 and V_5. The methane produced by the reaction was pumped away through T_2, and when all the reaction mixture had been pumped from the reaction vessel, the photometer was checked to see whether the two photocells were still balanced off against one another.

V_5 and T_2 were then closed, T_5 was opened, and a cardice-acetone bath put round trap 2. The bulb B had previously been filled with outgassed distilled water frozen down in liquid air. The HI distilled from the trap to the bulb, leaving the iodine and most of the methyl

iodide in the trap. Air was admitted to the traps section, trap 2 was removed, and its contents analysed for iodine as a check on the photometer. A clean trap 2 was put on the system, and, after pumping out the traps, the contents of the bulb B were allowed to warm up, the HI dissolving in the water. The bulb was removed and its contents analysed for HI, as described above.

CALCULATION OF THE RESULTS.

The experimental data obtained consisted of a record of light intensities at measured time intervals. From the calibration of the photometer, the light intensity measurements could be reinterpreted as iodine concentrations, and in the following discussion, this first step in the processing of the data will be taken for granted.

Besides this record of iodine formation, the temperature of the reaction vessel and the initial concentrations of the reactants were also required. The temperature was measured for each run using the chromel-P-alumel thermocouple. The initial concentration of HI was known directly from the titration of the HI from the reaction vessel after the run, and the stoichiometry of the reaction, since $(HI)_o = (HI)_t + (I_2)_t$ for the reaction

$$CH_3I + HI \longrightarrow CH_4 + I_2,$$

assuming $(I_2)_o$ is either zero or negligible.

The total number of moles of methyl iodide, n, distributed between reaction vessel and premixer bulb, was known from the equation

$$n = \frac{p}{760} \times \frac{v}{1000} \times \frac{1}{0.08205 \times T_B} \text{ moles},$$

where p = 141 mms. is the vapour pressure of methyl iodide at 0°C, v is the volume, 155 ccs., of the standard bulb between V_4 and V_6, and T_B is the absolute temperature of the water-jacket surrounding the bulb.

Thus, $n = 0.305 \times \frac{1}{T_B}$ moles.

In order to find what fraction of the methyl iodide had entered the reaction vessel, the assumption was made that the HI and CH_3I were completely mixed in the premixer, so that the HI distribution ratio between reaction vessel and premixer was the same as the methyl iodide ratio. Since the HI ratio was known from the titrations, the number of moles of CH_3I initially in the reaction vessel was given by

$$a.V = 0.305 \times \frac{1}{T_B} \times \frac{b.V}{\text{total moles HI in reaction vessel + premixer}}$$

where a and b are the initial concentrations, in moles per litre, of methyl iodide and HI respectively, in the reaction vessel, and V is the volume of the reaction vessel in litres.

<u>High Pressure Experiments.</u>

The data from this series of runs were interpreted on the basis of the kinetic scheme discussed previously, i.e.

$$CH_3I \longrightarrow CH_3 + I \text{ - initiating}$$

$$I + CH_3I \longrightarrow CH_3 + I_2 - \quad (1)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I - \quad (2)$$

$$CH_3 + HI \longrightarrow CH_4 + I - \quad (3)$$

$$I + I + M \rightleftharpoons I_2 + M$$

With steady-state assumptions, and assuming the unimolecular initiating step to be slow under the conditions used, the rate expression derived is

$$\frac{d(I_2)}{dt} = \frac{k_1 K^{\frac{1}{2}} (CH_3I)(I_2)^{\frac{1}{2}} . k_3(CH_3I)}{k_2(I_2) + k_3(HI)}$$

If $k_3(HI) \gg k_2(I_2)$, this reduces to

$$\frac{d(I_2)}{dt} = k_1.K^{\frac{1}{2}}.(CH_3I)(I_2)^{\frac{1}{2}} = k_{exp.}(CH_3I)(I_2)^{\frac{1}{2}}.$$

The above condition will hold if a large excess of HI is present.

On integration, (see Appendix I), this gives the equation

$$k_{exp.}\,t = 2\sqrt{a+m}\,(\tanh^{-1}\sqrt{\frac{x+m}{a+m}} - \tanh^{-1}\sqrt{\frac{m}{a+m}}),$$

where $a = (CH_3I)_o$, $m = (I_2)_o$, and x = the concentration of iodine produced by the reaction after time t, so that $(x + m)$ represents the total concentration of iodine present at time t.

Thus, if the proposed mechanism is correct, and the various assumptions are justified, a plot of $\tanh^{-1}\sqrt{\frac{x+m}{a+m}}$ against time should give a straight line of slope $\frac{1}{2} \cdot k_{exp.}\sqrt{a+m}$. The complete data for one run are listed in Table II, so that the method of testing the integrated rate equation can be explained. For this run, the furnace temperature was 561° K, a.V was 5.67×10^{-4} moles, b.V = $(HI)_o$ V was 4.22×10^{-2} moles. V, the volume of the reation vessel, was 2.40 litres, (see Appendix II).

TABLE II

Moles of iodine vs. time data for Run 76.

(x+m)V in moles x 10^{-6}. Time in seconds x 10^{-2}.

(x+m).V	Time	(x+m)V	Time	(x+m)V	Time
4.5	1.9	39.5	56.5	97.5	70.8
6	3.2	40.5	57.8	99	72
7	4.5	42.5	59	94.5	74.6
8	5.8	45	40.3	97.5	77.2
9.5	7.1	46.5	42.0	100	79.4
11	8.3	48	44.2	103.5	80.7
12	9.7	50	45.4	104.5	81
13.5	10.9	51.5	46.7	106	83.2
14.5	12.2	53.5	48.0	107.5	85.6
15.5	13.4	55	49.2	110.5	84.9
17	14.7	56	50.5	114	86.1
18	16.0	58	51.8	116	88.8
19	17.3	60.5	53	120.5	91.2
20.5	18.6	62	54.5	123	93.4
22.5	21.2	65.5	55.6	126	95.7
24.5	22.4	65	56.8	129.5	96.2
25.5	25.7	67	58.1	151.5	97.5
27	25	71	60.7	135	98.8
29	26.3	73	61.9	135.5	100
30.5	27.6	75.5	65.2	137.5	101.5
32	30.1	78.5	63.7	144	105.0
34.5	32.7	80.5	67	145	105.1
36.5	33.9	85	69.5		

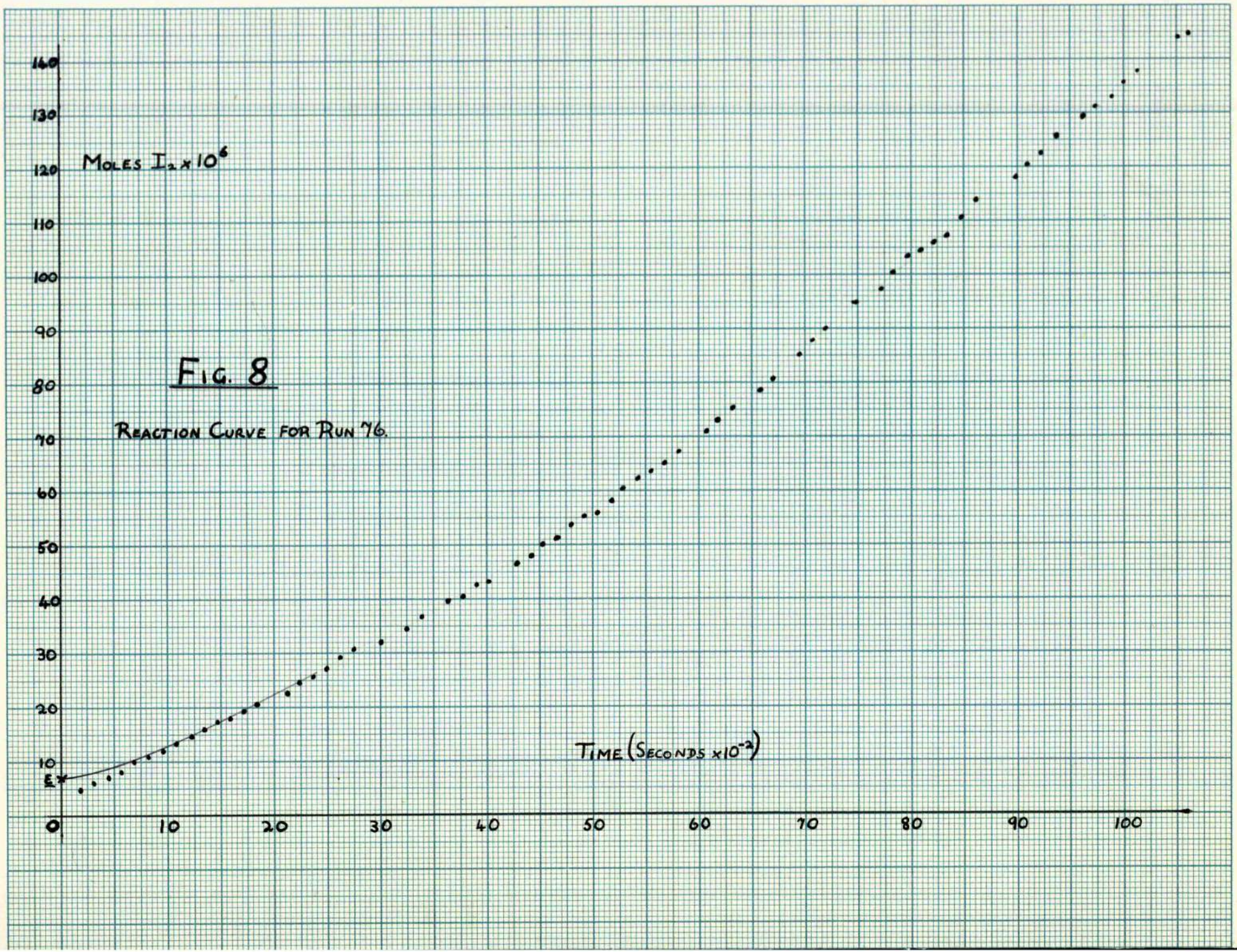


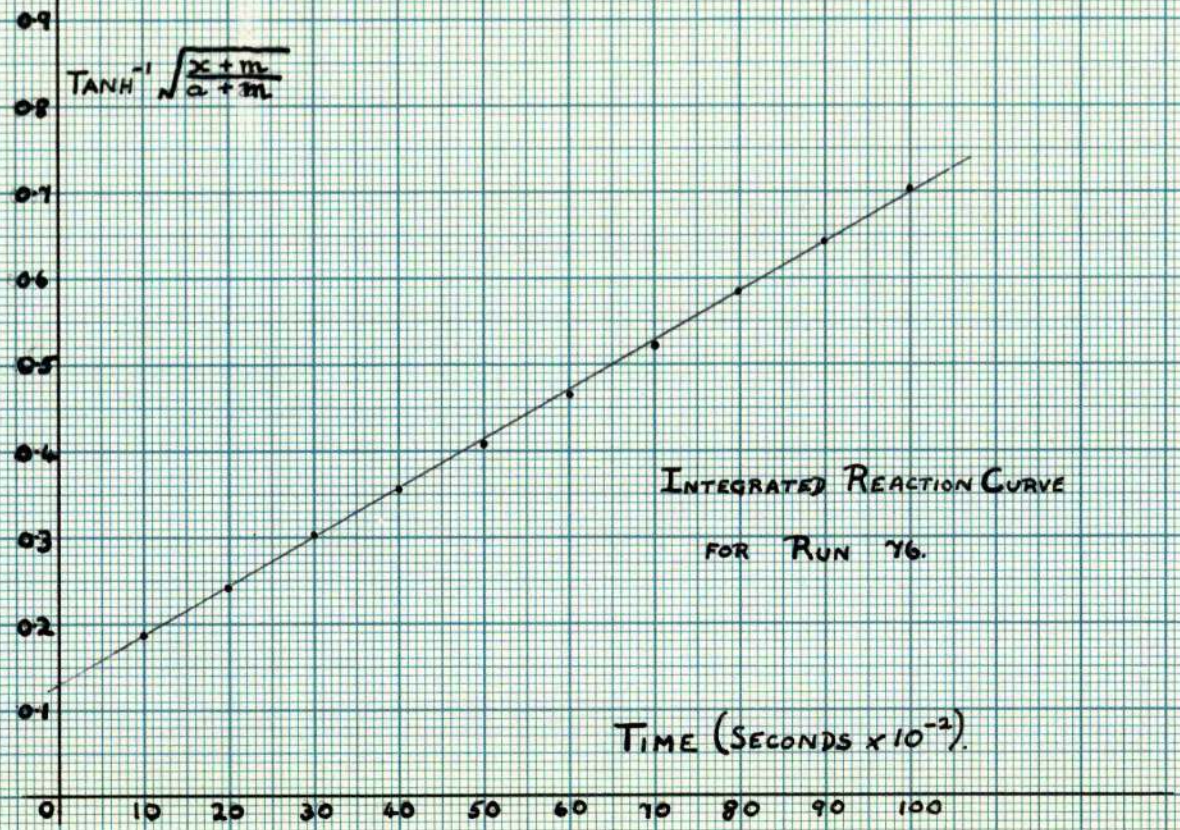
FIG. 8

REACTION CURVE FOR RUN 76.

The curve obtained on plotting (x+m)V against time is shown in Fig. 8. The shape of the curve is typical of an autocatalytic reaction, the rate accelerating as reaction proceeds. The very early portion of the curve tails off to zero, this presumably corresponding to a period in which the reaction gases were warming up and the system settling down generally. By smoothly extrapolating the reaction curve back to t = o, the intercept on the (x+m)V axis could be estimated, this giving the value of mV. This was usually found to be of the order of 10×10^{-6} moles. Pains were taken to try to ensure that there was no iodine present in the reaction mixture. Thus, the HI was distilled repeatedly, as was the methyl iodide, with no apparent effect on the general trend of the values of mV. This small amount of iodine probably arose from some slight decomposition of one or both of the reactants while mixing, though a few runs were done with varying mixing times, with no evidence of any correlation between mixing time and the value of m. It was eventually realised that a small positive value for m was in fact of benefit, as without it the initiation of the autocatalytic reaction would depend entirely on the unimolecular fission of the CH_3I, with a resulting complication of the rate expression.

Thus, for run 76, the value of mV was 7×10^{-6} moles, so that (a+m)V was 5.74×10^{-4} moles. Values of (x+m)V and t were read off the smoothed reaction curve, and treated as indicated in Table III.

Fig. 9.



Integrated Reaction Curve

for Run 76.

TABLE III

Calculation of integrated rate function for Run 76 $(x+m)V$ in moles x 10^{-6}. t in seconds.

t (secs.)	$(x+m)V$	$\frac{x+m}{a+m}$	$\sqrt{\frac{x+m}{a+m}}$	$\tanh^{-1}\sqrt{\frac{x+m}{a+m}}$
1000	15	.035	.187	.189
2000	21.5	.057	.239	.245
3000	32	.086	.293	.302
4000	45.5	.116	.341	.356
5000	56	.150	.387	.408
6000	70.5	.189	.435	.466
7000	86	.230	.480	.525
8000	105	.275	.524	.584
9000	120	.321	.567	.643
10000	138	.369	.607	.704

The values of the square roots and inverse hyperbolic tangents were obtained from the "Handbook of Chemistryand Physics"[62]. The plot of $\tanh^{-1}\sqrt{\frac{x+m}{a+m}}$, shown in Fig. 9, is a good straight line, of slope 0.572×10^{-4}.

$$\text{Then } k_{exp.} = \text{slope} \times 2/\sqrt{a+m} = \frac{0.572 \times 10^{-4} \times 2}{(5.74 \times 10^{-4}/V)^{\frac{1}{2}}}$$

$$\text{i.e. } k_{exp.} = 0.918 \times 10^{-2} \text{ litres}^{\frac{1}{2}} \text{ moles}^{-\frac{1}{2}} \text{ seconds}^{-1}.$$

Temperature Dependence of $k_{exp.}$

In all, 29 high-pressure runs similar to Run 76 have to be reported, some involving as many as 120 experimentally determined points, and some condensation of this data is desirable. Since the object of performing this number of experiments was to determine the nature of the temperature dependence of $k_{exp.}$, Table IV below lists for each run only the temperature and the value calculated for $k_{exp.}$ In Appendix III are collected more complete data, giving values of $(CH_5I)_o$, $(HI)_o$, $(I_2)_o$, T^oK, and values of (I_2) at stated time intervals, read off the smoothed reaction curves. These quoted values of $(I_2)_t$ number about 12 for each run, but are in fact derived from curves defined by many more points. The values calculated for $\tanh^{-1}\sqrt{\frac{x+m}{a+m}}$ are also given. The fastest runs gave curves involving about 45 points, the slowest over 100.

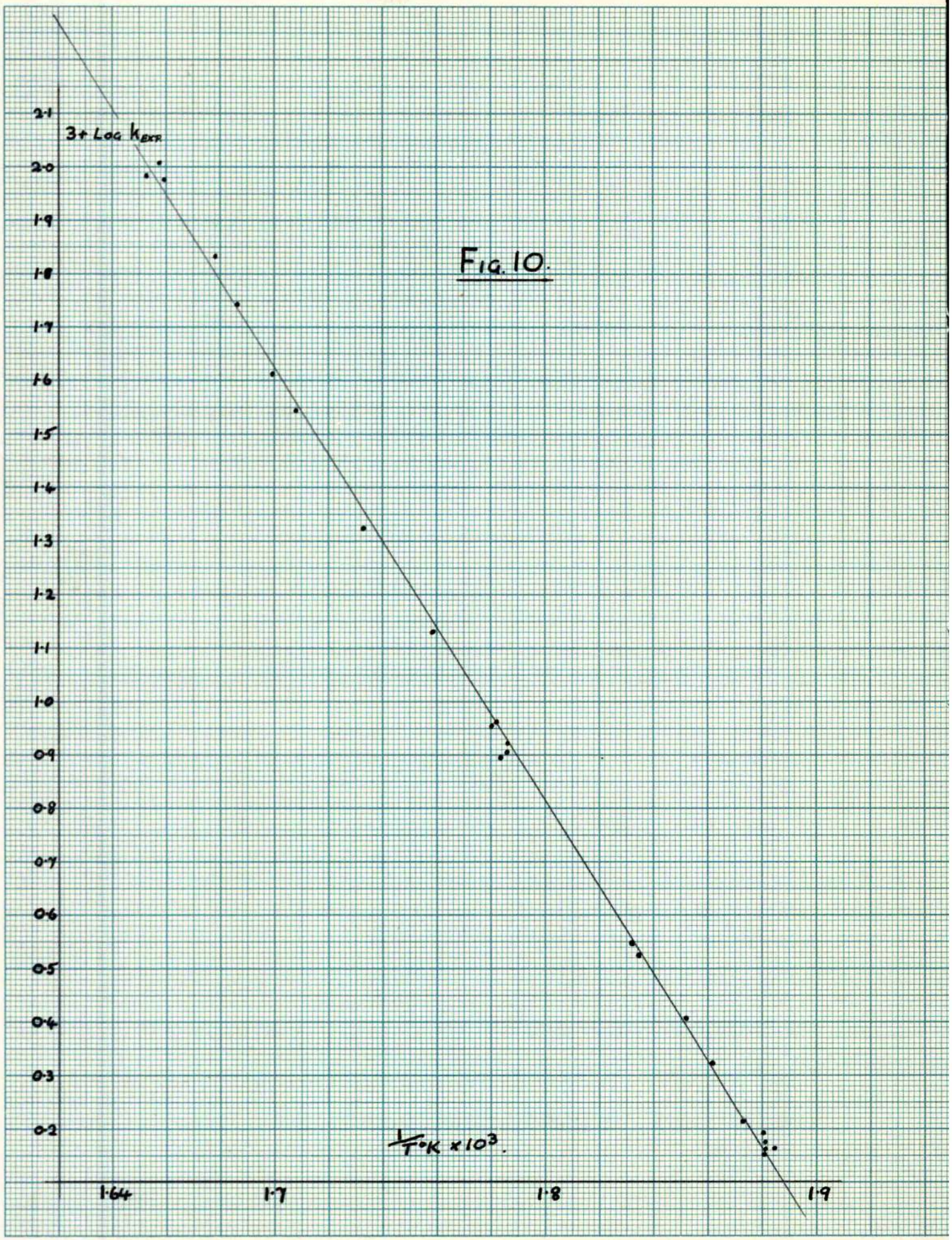

3+ Log k_{exp}
2·1
2·0
1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
1·64
1·7
1·8
1·9
$\frac{1}{T°K} \times 10^3$.

FIG. 10.

TABLE IV

Collected results of high-pressure runs. $k_{exp.}$ in litres$^{\frac{1}{2}}$.moles$^{-\frac{1}{2}}$. seconds^{-1}. 10^{-3}.

Run	T°K	$k_{exp.}$	Run	T°K	$k_{exp.}$
55	546	3.55	70	595	55.7
56	545	3.36	71	596	68.8
57	540	2.57	72	602.5	95.9
58	537	2.15	73	603	102.3
59	532	1.57	74	605	III blank
60	550.5	1.46	75	605	97.6
61	551.5	1.45	76	563	9.18
62	551.5	1.45	77	560	8.04
63	551.5	1.51	78	563.5	9.15
64	554	1.64	79	560.5	7.89
65	560	3.37	80	560	7.73
66	568.5	13.5	81	560	7.94
67	577	21.6	82	560	7.85
68	585.5	35.5	83	561	8.45
69	588.5	41.0			

The Arrhenius plot of log k_{exp} against 1/T is shown in Fig. 10, the temperature range being 74.5°K. The plot appears to display a slight curvature, but can be well represented by a straight line given by log k_{exp} = 12.37 - 56,960/4.57.T.

Verification of Kinetic Scheme.

A discussion of the reaction mechanism is included in this section describing the calculation of the results, since the fashion in which the data was treated arose from the assumptions made for the kinetic scheme, and some justification for these assumptions seems necessary at this stage.

The fact that the values of $k_{exp.}$, derived from the data by the method described, do in fact give a good Arrhenius plot, is strong evidence in favour of the mechanism being essentially correct. More direct evidence can be adduced, as shown below.

Overall Stoichiometry of the Reaction.

Ogg[1] has shown that for methyl, ethyl, and n-propyl iodides, the reaction with HI proceeds exclusively according to the overall equation

$$RI + HI \longrightarrow RH + I_2.$$

No check on this was made during the present investigation, as Ogg's demonstration was fairly conclusive.

Homogeneity of the reaction at high pressures.

A more complete discussion of this point is more conveniently postponed until the results of the low-pressure experiments have been given. It is sufficient to state here that, again following the findings of Ogg,[1] the high pressure experiments were assumed to proceed by a homogeneous gas-phase mechanism.

Dependence of the rate of HI concentration.

An important assumption made in the above treatment of the

experimental data was that the HI concentration was high enough for reaction (5) to predominate largely over reaction (2), i.e. $k_5(HI) \gg k_2(I_2)$.

If this condition is fulfilled, the reaction rate must be independent of HI concentration, since the role of this reactant is presumed to be that of a radical-catcher. If this is so, variations in HI concentration above a certain limit should not affect the reaction rate, the limiting rate corresponding to a condition where there is sufficient HI present to remove practically all the CH_3 radicals from the system. Table VI lists the results of a series of runs at practically constant temperature and $(CH_3I)_o$, with varying values of $(HI)_o$.

TABLE VI

Effect on rate of varying $(HI)_o$.

Run	T^oK	$a.V.10^4$ moles	$b.V.10^2$ moles	$k_{exp.}\ 10^5$
65	560	5.67	1.66	8.57
77	560	5.68	0.87	8.04
80	560	5.70	2.35	7.73
81	560	5.62	2.96	7.94
82	560	5.70	2.05	7.85
85	561	5.60	1.53	8.45

Fig. 11

Variation of $k_{exp.}$ with $(HI)_o$

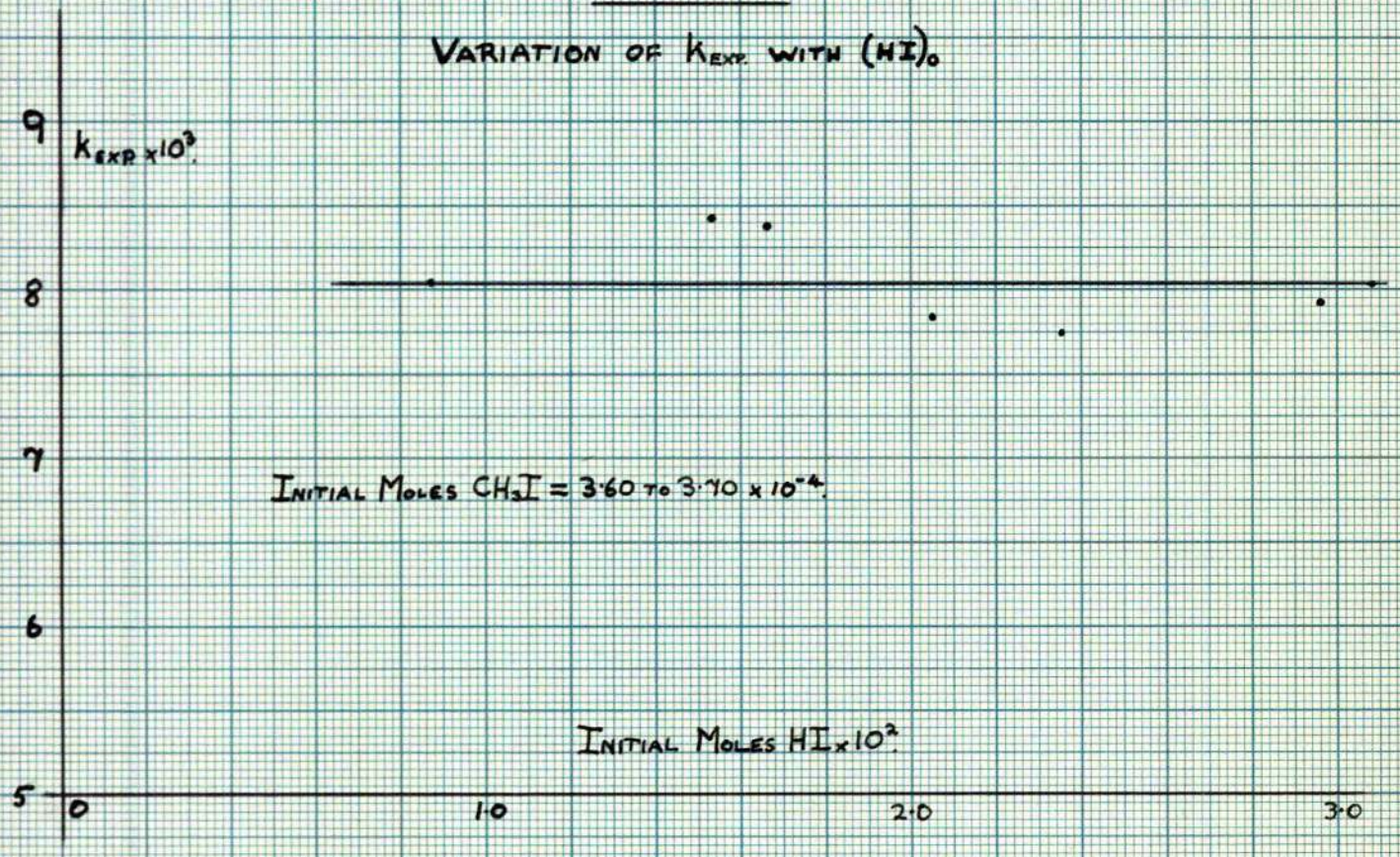


Fig. 12.

Integrated Reaction Curves
For Runs 68 and 70.

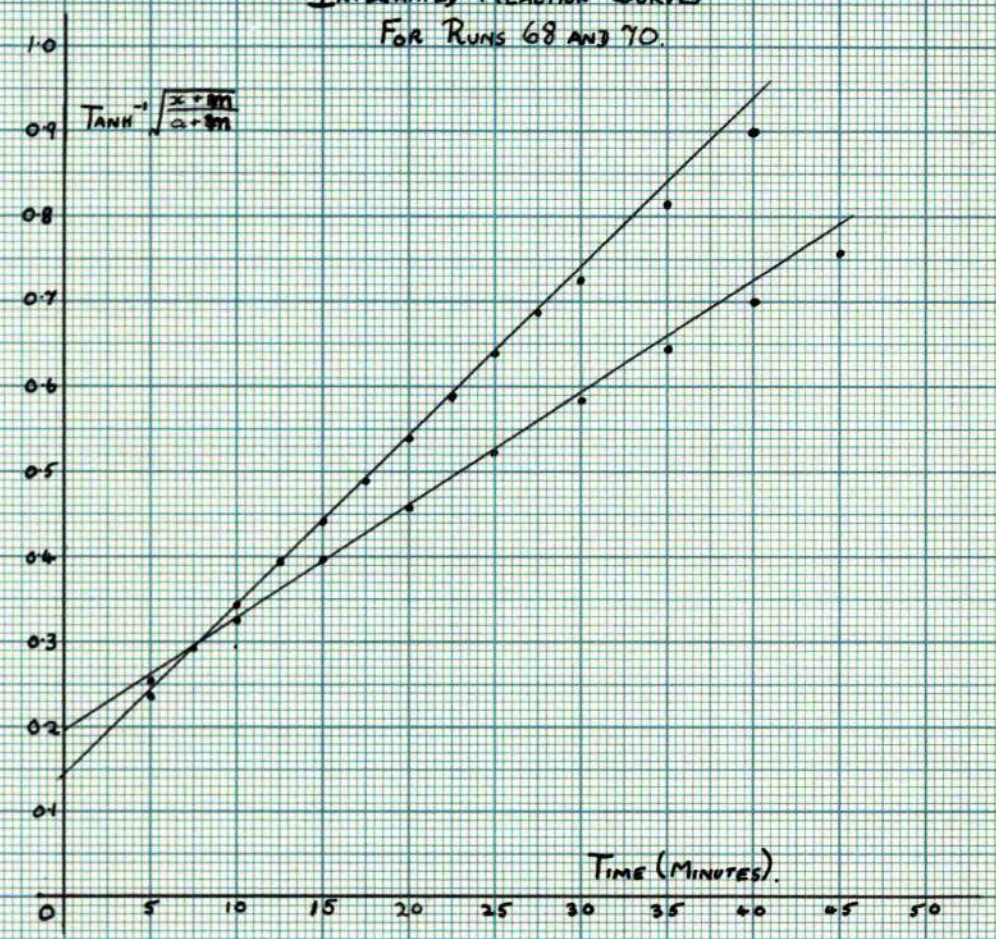


Fig. 11 shows $k_{exp.}$ plotted against $(HI)_o.V$. The latter parameter was varied by a factor of over 5, with no apparent effect on the values of $k_{exp.}$, so it seems safe to conclude that, under the conditions used of excess HI, the reaction is of zero order with respect to this component, as found by Downs[2] and Gow[5] for CF_3I and benzyl iodide, respectively.

However, on examination of the integrated plots for some of the runs with lower values of $(HI)_o$, which were followed to higher percentages of reaction, it can be seen that the later points tend to fall below the straight line defined by the rest of the data. This would indicate that, in these cases, the assumption that $k_5(HI) \gg k_2(I_2)$ becomes untenable at higher conversions of the iodide to iodine. In Fig. 12 are shown the graphs of the integrated functions for Runs 68 and 70, which exhibit this behaviour. The values of $k_{exp.}$ quoted in Table IV for these runs were calculated from the slopes of the early parts of these plots, indicated in Fig. 12.

Dependence of the rate on methyl iodide concentration.

All injections of methyl iodide consisted of only one filling of the standard volume, except for Runs 78 and 79, which involved two and three fillings respectively. Table VII lists the relevant data for these runs, together with the data for comparable experiments.

TABLE VII

Effect on rate of varying $(CH_3I)_o$

Run	T°K	a.V.10^4moles	b.V.10^2moles	$k_{exp.}10^5$
76	565	3.67	4.22	9.18
78	565.5	7.22	2.44	9.15
79	560.5	11.03	2.06	7.89
82	560	3.70	2.05	7.85
85	561	3.60	1.53	8.45

Since the values of b.V in each of these runs was large enough for the experiments to be well within the region of independence of the rate of III, the variations in this parameter can be neglected.

Run 78 had double the value of a.V of Run 76, performed at the same temperature, and the values of $k_{exp.}$ derived on the basis of the proposed mechanism, agree closely, the closeness of the agreement not being typical of the reproducibility of $k_{exp.}$ Similarly, the values of $k_{exp.}$ for Runs 79, 82 and 85 are in agreement, Run 79 having a value of a.V about three times as large as that of the other two. Thus, the proposed first-order dependence of the rate on methyl iodide concentration appears to be justified.

Behaviour of III alone under Reaction Conditions.

There was a possibility that the rate of decomposition of III

alone might be significant under reaction conditions. Run 74 was an HI blank, carried out in exactly the same manner as the other runs, except that no methyl iodide was injected. As quoted in Appendix III, there appeared to be initially 5 x 10^{-6} moles of iodine in the reaction vessel with the HI, which increased to 5.5 x 10^{-6} moles by the end of the run. Since the temperature used was that of Run 75, at the top of the temperature range, and the time for which the blank was allowed to proceed was twice that for Run 75, the decomposition rate of HI is not significant under the conditions used.

Agreement of Photometer with Iodine Titration.

The largest amount of iodine measured by the photometer during the high pressure runs was 190 x 10^{-6} moles. (Appendix III, Run 72). It was assumed that the calibration of moles of iodine vs. log $(1 - I_{abs}/ I_o)$ was linear up to this point, which seems justifiable from an inspection of Fig. 5. The iodine produced in the reaction was always estimated by titration with thiosulphate as a check on the final photometer reading. In all cases except Runs 57, 60 and 77, the two estimates agreed reasonably well, the values obtained by titration lying in a region 5% above to 6% below the photometer measurements.

The discrepancies observed for runs 57, 60, and 77 were 20%, 12%, and 20% respectively, all the titration values being too low. These errors are somewhat disastrous, but since the photometer

readings were all in line with those expected from other runs at similar temperatures, it was decided that some mistake must have been made in the titrations.

Low Pressure Experiments.

Some experiments were performed under conditions where the rate was not expected to be independent of the HI concentration. The total pressures used in this series of runs were of the order of 50 mms., with the HI : CH_3I ratios about 5 or 4 to 1.

As in the case of the high-pressure experiments, there is too much data to be conveniently reported in full. As before, one run will be completely reported, and the other data suitably condensed. Run 97 was chosen to be reported in full, as it was one of the fastest runs performed, thus involving the fewest number of points determined.

The temperature was 597.5°K, $(CH_3I)_o.V$ was 715 x 10^{-6} moles, and $(HI)_o$ was 2270 x 10^{-6} moles.

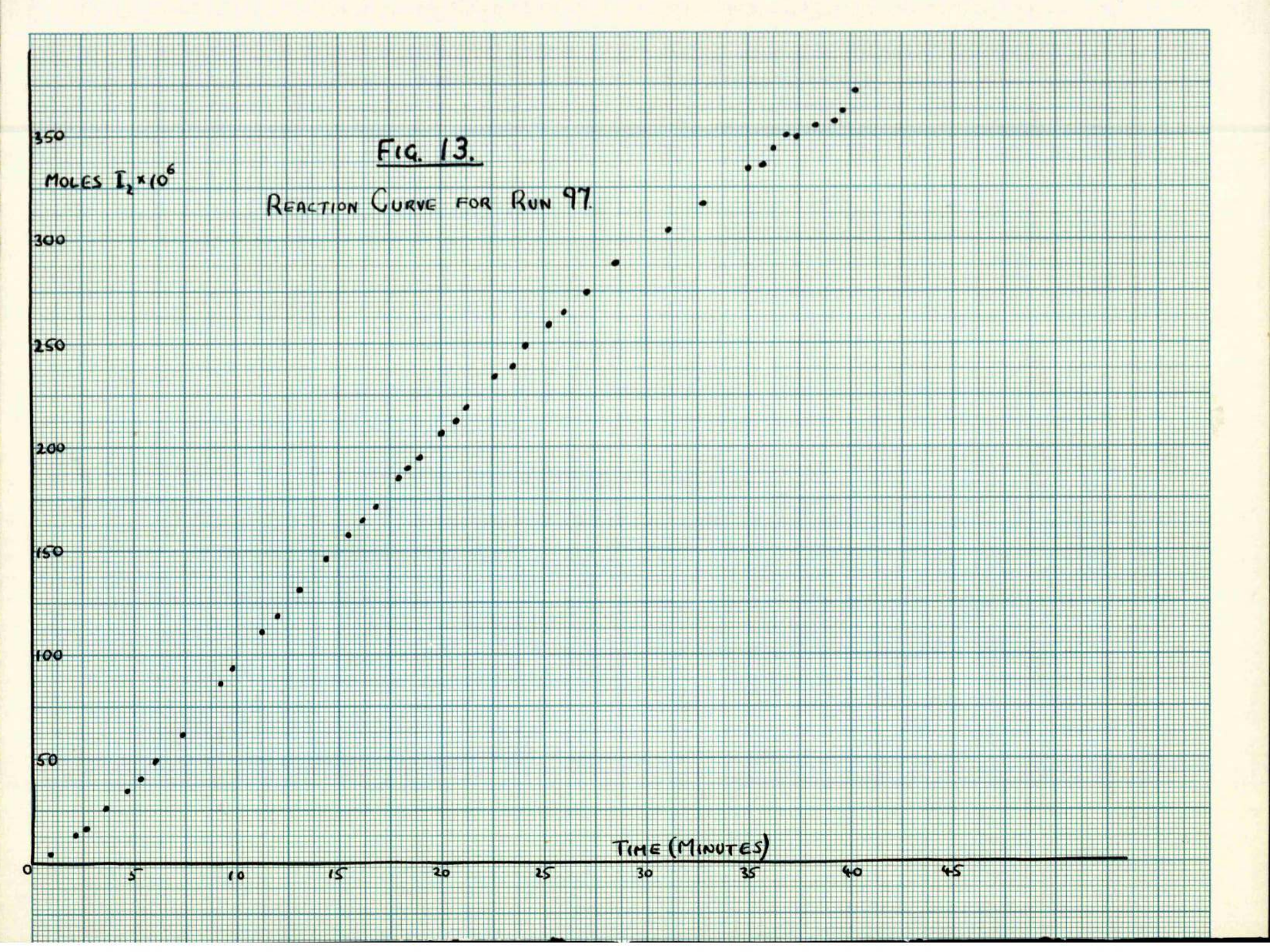


FIG. 13.
REACTION CURVE FOR RUN 97.
MOLES $I_2 \times 10^6$
350
300
250
200
150
100
50
0
5
10
15
20
25
30
35
40
45
TIME (MINUTES)

TABLE VIII

Moles of iodine vs. time data for Run 97. $(x+m)V$ in moles $\times 10^{-6}$. Time in minutes.

$(x+m)V$	Time	$(x+m)V$.	Time	$(x+m)V$	Time
4	0.8	158	15.4	289	28.4
13	2.2	166	16.1	305	51.1
17	2.6	171	16.8	301	51.6
27	3.7	186	17.9	319	52.8
35	4.7	190	18.4	334	53.4
41	5.3	195	19	354	53.9
55	6.4	208	20	334	55.1
62	7.3	215	20.7	356	55.7
74	8.3	220	21.3	343	56.2
86	9.2	254	22.7	350	56.8
94	9.8	259	23.5	350	57.4
111	11.3	249	24.1	355	58.3
118	11.9	260	25.3	357	58.9
132	13.1	264	25.9	361	59.5
146	14.3	275	27.1	374	40.2

This data is plotted in Fig. 15. The lowest part of the graph has the shape typical of an autocatalytic reaction curve, but this falls off later, and the rate begins to deccelerate with increasing iodine production.

The method used to interpret this reaction curve was that due to Benson and O'Neal.[54] Recasting the rate equation

$$\frac{d(I_2)}{dt} = \frac{k_1 K^{\frac{1}{2}} \cdot (CH_3I)(I_2)^{\frac{1}{2}} \cdot k_3(HI)}{k_2(I_2) + k_3(HI)}$$

into the form $R_{I_2} = \frac{k_1 K^{\frac{1}{2}} \cdot (CH_3I)(I_2)^{\frac{1}{2}}}{1+(k_2/k_3) \cdot (I_2)/(HI)}$, where $R_{I_2} = \frac{d(I_2)}{dt}$

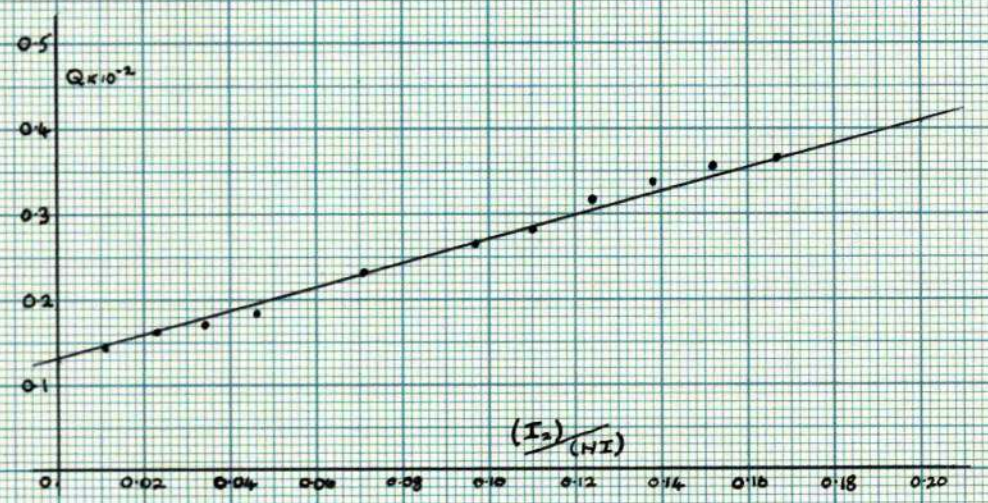
and rearranging, gives $Q = \frac{(CH_3I)(I_2)^{\frac{1}{2}}}{R_{I_2}} = (1/k_1 K^{\frac{1}{2}}) \left[1+(k_2/k_3)(I_2)/(HI)\right]$

Knowing the initial concentrations, and reading the instantaneous values of (I_2) from the smoothed reaction curve, all the concentration factors in this equation could be evaluated from the stoichiometry of the reaction. The values of R_{I_2} were measured as the slopes of the reaction curve at the appropriate points. The technique used was to hold a mirror standing vertically on the graph paper, so that the bottom edge of the mirror intersected the curve at the point at which the value of R_{I_2} was required. The mirror was then rotated about this point until, on looking into the mirror, the graph and its reflection were seen as one continuous curve. In this position, the mirror was lying along the normal to the curve. Although there is a certain subjective element in this method, it is probably the most reliable technique available.

A plot of the values of the function Q so derived against the ratio $(I_2)/(HI)$ should give a straight line, of intercept $1/k_1 . K^{\frac{1}{2}}$,

FIG. 14.

Q VS. $\frac{(I_2)}{(HI)}$ FOR RUN 9Y.



and slope $(1/k_1.K^{\frac{1}{2}})$ X (k_2/k_3). Table IX demonstrates how these functions were calculated. The seventh column, $Q.V.^{\frac{1}{2}}10^5$, was obtained by dividing the product of the fourth and fifth columns by the corresponding entry in the sixth column. The value of $V^{\frac{1}{2}}$ is $\sqrt{2.40} = 1.550$ litres$^{\frac{1}{2}}$. Concentrations are in moles per litre, and R_{I_2} is in moles litres^{-1} seconds^{-1}.

TABLE IX

$[(I_2).10^6.V]$	$[(III).10^6.V]$	$\frac{[(I_2)]}{[(III)]}$	$[(CH_3I).10^6.V.]$	$[(I_2^{\frac{1}{2}}.10^5.V^{\frac{1}{2}})]$	$[R_{I_2}.10^6.V.]$	$Q.V^{\frac{1}{2}}10^5$	$Q.10^{-2}$
25	2245	.011	690	5.00	.152	$.227X10^5$	.146
50	2220	.025	665	7.07	.189	$.249X10^5$	.161
75	2195	.034	640	8.66	.209	$.265X10^5$	.171
100	2170	.046	615	10.00	.214	$.287X10^5$	.185
150	2120	.071	565	12.25	.193	$.359X10^5$	.252
200	2070	.097	515	14.14	.177	$.411X10^5$	.265
225	2045	.110	490	15.00	.169	$.455X10^5$	.281
250	2020	.124	465	15.86	.149	$.495X10^5$	.319
275	1995	.158	440	16.58	.159	$.525X10^5$	.339
300	1970	.152	415	17.32	.130	$.555X10^5$	.357
325	1945	.167	390	18.03	.125	$.565X10^5$	.363

The graph of Q against $(I_2)/(III)$ is shown in Fig. 14. It is a reasonable straight line, the intercept on the Q-axis being $0.130X10^2$,

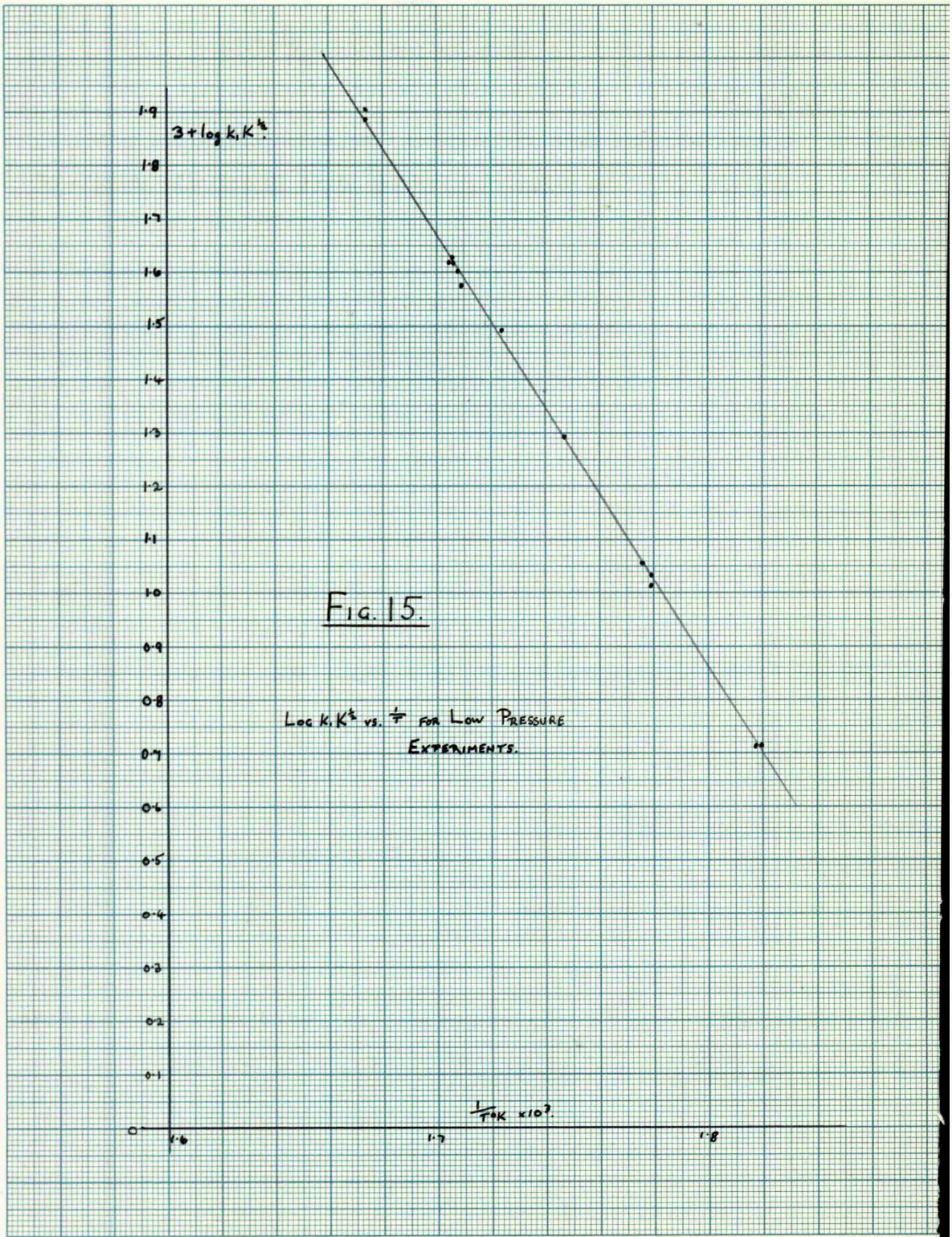


FIG. 15.

LOG K, K½ VS. $\frac{1}{T}$ FOR LOW PRESSURE EXPERIMENTS.

and the slope $1.39X10^{2}$. These values give $k_1K^{\frac{1}{2}}=7.7X10^{-2}$, and $k_2/k_3= 10.7$.

The summarised data of the other low-pressure runs are given in Appendix IV. The times required for about 12 definite amounts of iodine to be produced are quoted, having been read off smoothed reaction curves defined by as many as 160 experimentally determined points. The corresponding values calculated for Q are also given.

In Table X are listed the temperature, the value of k_1/k_3, for each run.

TABLE X

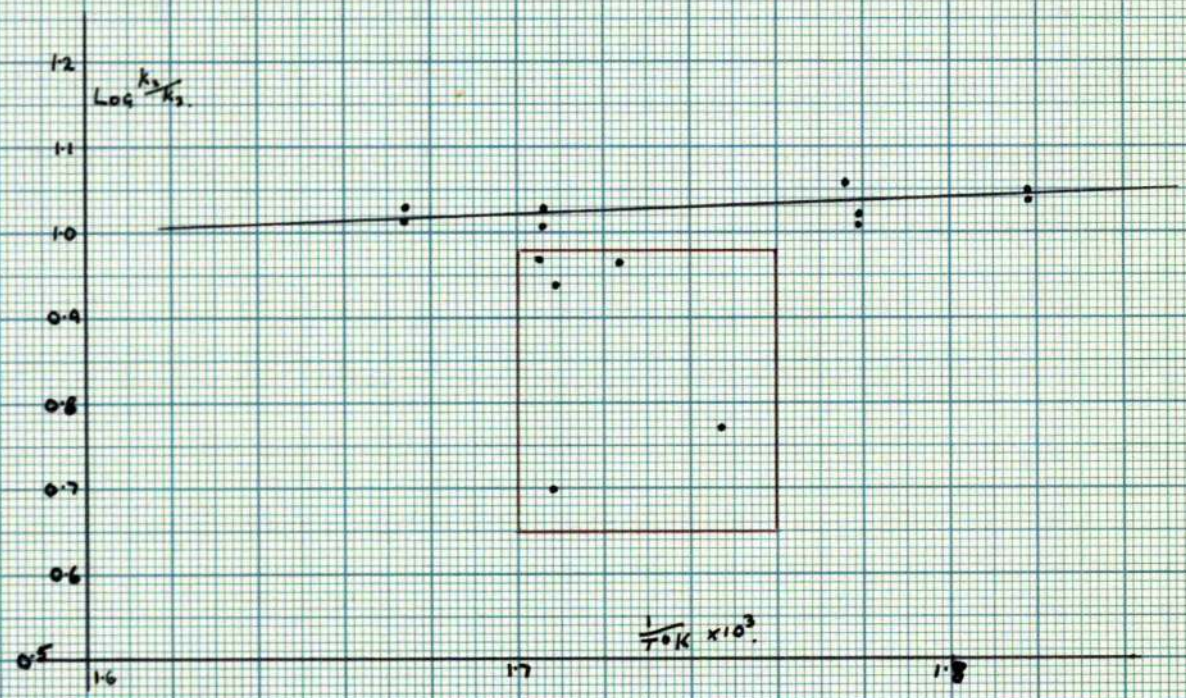
Collected Results of Low Pressure Runs.

Run	$T^{o}K$	$k_1K^{\frac{1}{2}}X10^{3}$	k_2/k_3	Run	$T^{o}K$	$k_1K^{\frac{1}{2}}X10^{3}$	k_2/k_3
85	565	11.4	11.4	92	586.5	41.7	9.5
86	572.5	19.6	5.9	93	550	5.2	11.2
87	580	31.3	9.2	94	549.5	5.2	10.9
88	585.5	40.0	5.0	95	562	10.3	10.5
89	585	37.7	8.7	96	562	10.8	10.2
90	586	42.6	10.7	97	597.5	77.0	10.7
91	586	41.7	10.2	98	597.5	80.0	10.3

The Arrhenius plot of $\log k_1K^{\frac{1}{2}}$ is shown in Fig. 15. Over the temperature range of $48^{o}K$, it gives a fairly good straight line, given by $\log k_1K^{\frac{1}{2}} = 12.45 - 37,040/4.57.T$ This is in good general

FIG. 16

LOG $\frac{k_2}{K_2}$ VS. $\frac{1}{T}$, PRESENT WORK ONLY.



agreement with the expression for $k_{exp.}$ from the high pressure runs, though the A-factor seems to be about 10% higher than in the latter case.

The values obtained for the ratio k_2/k_5 are not nearly as satisfactory. The Arrhenius plot is shown in Fig. 16, and this clearly exhibits the scatter of the data. If the results of runs 86, 87, 88, 89 and 92 are arbitrarily ignored, a reasonable straight line can be drawn through the remaining points, giving $k_2/k_5 = 4.8.e^{+\frac{910}{RT}}$. These values of the Arrhenius parameters are of the expected order of magnitude, but are obviously not entirely reliable, due to the rejection of the results of five of the experiments.

Agreement of photometer with iodine titration for low-pressure experiments.

Due to the larger scatter of the photometric data at high iodine concentrations, caused in turn by the logarithmic nature of the absorption law and the resultant crowding of the upper part of the scale, the two methods of iodine estimation at the end of a run did not agree as closely as for the high-pressure runs. However, the agreement was within 6 to 7%, with a definite tendency for the titration to give a higher value than the photometer.

DISCUSSION

The reaction mechanism postulated to account for the kinetics of the thermal reaction between methyl iodide and hydrogen iodide is shown below:

$$I + CH_3I \longrightarrow CH_3 + I_2 \qquad (1)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (2)$$

$$CH_3 + HI \longrightarrow CH_4 + I \qquad (3)$$

$$I + I + M \rightleftharpoons I_2 + M$$

The suggestion that the reaction is catalysed by iodine is supported by comparing the results of runs 62 and 65. These runs produced 59.5×10^{-6} and 23.5×10^{-6} moles of iodine, respectively, in 18,000 seconds, all parameters being practically identical in the two cases except for the values of $(I_2)_o$. Run 62, for which 12×10^{-6} moles of iodine were originally present, did not have to work its way through the slow initial induction period, whereas run 65, with only 6×10^{-6} moles of iodine initially, did have to build up its rate slowly.

At high concentrations of HI, the rate became independent of this variable. The above reaction scheme accounts for this behaviour, on the basis of an excess of HI removing practically all of the methyl radicals, thus preventing the back reaction (2). The fact that the

rate eventually becomes zero order with respect to HI rules out the four-centre reaction

$$CH_3I + HI \longrightarrow CH_4 + I_2 \quad (4),$$

suggested by Ogg[1], as this would require a first-order dependence on HI. Theoretical considerations relevant to the occurrence of (1) or (4) as the preferred route are discussed in a later section. These support the evidence given here in favour of (1).

The autocatalysis implicit in the scheme (1),(2), (3) requires as initiating step the dissociation

$$CH_3I \longrightarrow CH_3 + I$$

The contribution of this unimolecular fission of methyl iodide has been assumed to be negligible under the experimental conditions of the present work. This can be shown as follows.

If Ru is the unimolecular rate of disappearance of CH_3I, and Rc the rate of the catalytic contribution, then

$$\frac{Ru}{Rc} = \frac{ku\,(CH_3I)}{k_{exp.}(I_2)^{\frac{1}{2}}(CH_3I)} = \frac{ku}{k_{exp.}(I_2)^{\frac{1}{2}}},$$

for the high-pressure experiments.

Assuming a reasonable value of ku of $10^{13} \cdot e^{-54,000/RT}$ secs.$^{-1}$, and inserting for $k_{exp.}$ the value found,

$k_{exp.} = 10^{12.4} \cdot e^{-57,000/RT}$ litres$^{\frac{1}{2}}$ moles$^{-\frac{1}{2}}$ secs.$^{-1}$, gives

$$\frac{Ru}{Rc} = \frac{10^{0.6} \cdot e^{-17,000/RT}}{(I_2)^{\frac{1}{2}}}.$$

The atomic reaction rate will be lowest at the lowest iodine concentrations, say 10^{-6} moles per litre, and the unimolecular contribution highest at the top of the temperature range, 600°K. Then,

$$\left(\frac{Ru}{Rc}\right)_{max.} = 10^{-2.6}$$

This figure drops to $10^{-3.6}$ when 100 X 10^{-6} moles of iodine are present, so that neglect of the unimolecular fission rate seems justifiable.

The same conclusion can be shown to hold for the low-pressure experiments, since the average autocatalytic rate during a low-pressure run is less than that for a high-pressure run at the same temperature by a factor $1/(1 + \frac{k_2(I_2)}{k_5(HI)})$. Since k_2/k_5 is of the order of 10, and $(I_2)/(HI)$ had an average value of 0.1, this factor is about 0.5, so that for the low-pressure runs, $(Ru/Rc)_{max.} = 2 \times 10^{-2.6} = 10^{-2.3}$.

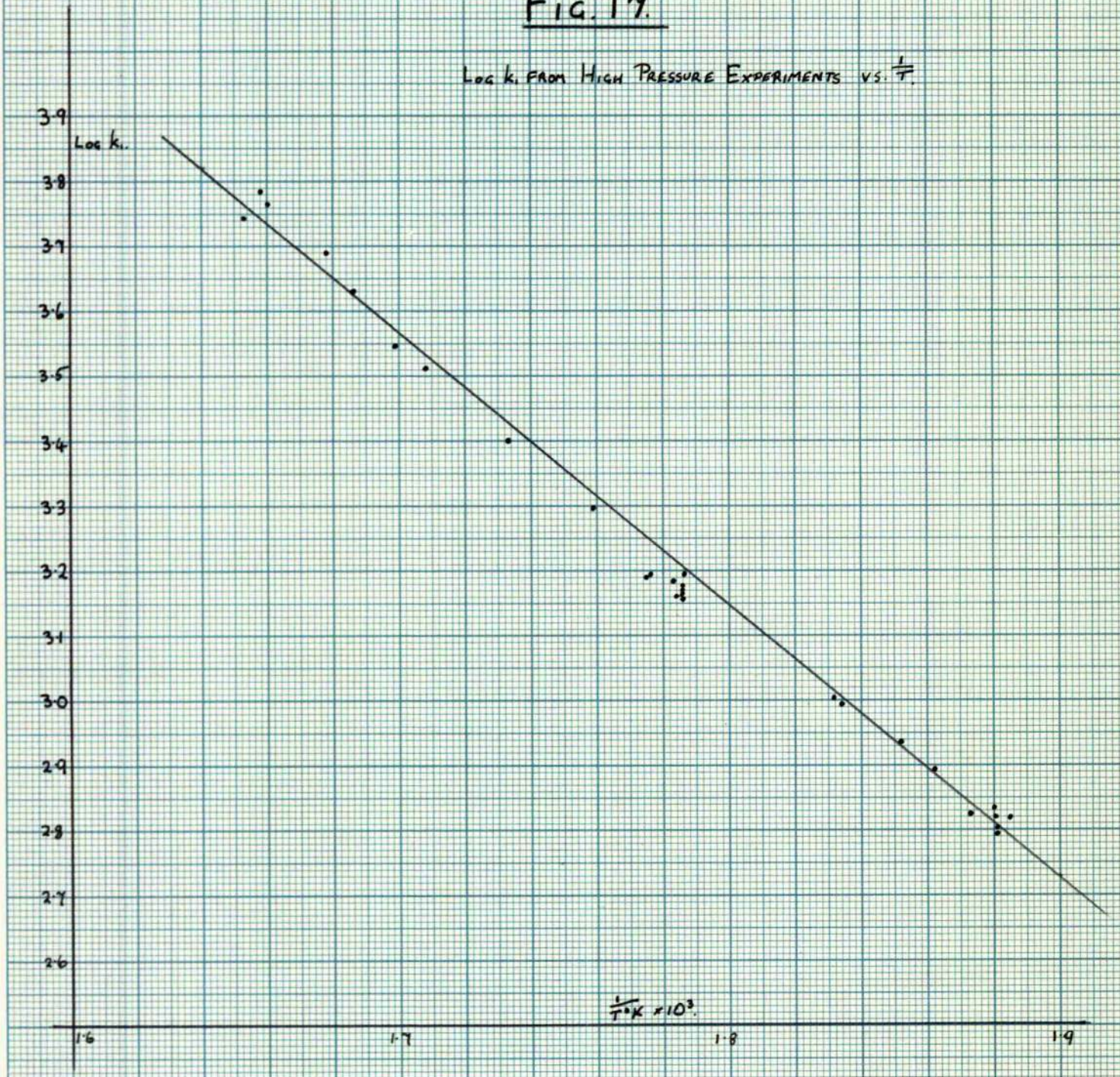
Evaluation of the rate constant k_1.

The rate constant $k_{exp.}$ derived from the high-pressure runs is identifiable with the product $k_1 K^{\frac{1}{2}}$, according to the present kinetic analysis. The corresponding rate constant derived from the low-pressure experiments was explicitly referred to as $k_1.K^{\frac{1}{2}}$, in order to conveniently distinguish between the two independently obtained quantities.

To obtain a value of k_1 from either set of data requires a knowledge of K, the equilibrium constant for the iodine dissociation

FIG. 17.

LOG k. FROM HIGH PRESSURE EXPERIMENTS VS. $\frac{1}{T}$.



equilibrium. The data of Perlman and Rollefson[69] were used to calculate an expression for the temperature dependence of K. (See Appendix V). The expression derived is:

$$\log K = -7,788/T - 0.093 \log T + 5.622,$$

where K is the equilibrium constant in moles per litre for the equilibrium $I_2 \rightleftharpoons 2I$.

The corresponding value of $\frac{1}{2} \log K$ was subtracted from each experimentally obtained value of $\log k_1 K^{\frac{1}{2}}$, andthe resulting values of $\log k_1$ from the high-pressure runs are shown plotted against $\frac{1}{T}$ in Fig. 17. When worked out statistically, the plot can be represented by the linear relation $\log k_1 = (10.71 \pm 0.08) - (19,200 \pm 200/4.57.T)$.

The low-pressure data, when treated in the same way, give an expression

$$\log k_1 = (10.78 \pm 0.12) - (19,200 \pm 300/4.57.T).$$

It was felt that the pre-exponential factor obtained from the high-pressure experiments was probably the more reliable, as any spurious surface effects are less likely to operate in a high-pressure system. The activation energies obtained for this elementary reaction by the two different methods are in excellent agreement. Thus, at 568°K, the mean temperature of the range investigated, the rate constant for the reaction $I + CH_3I \longrightarrow CH_3 + I_2$ (1) is given by $\log k_1 = 10.71 - 19,200/4.57.T$.

Evaluation of the ratio k_2/k_3.

The Arrhenius plot of $\frac{1}{T}$ against the values of log k_2/k_3 obtained in the present work, (Fig. 16), shows a large scatter of the data, even when the five doubtful runs are ignored. An extension of the temperature range is obviously desirable, and this is available from the results obtained by Benson and O'Neal[68] for the photolysis of acetone in presence of HI.

Their results are listed in Table XI, together with the values obtained in the present work. These latter values are lower than those quoted in Table X. Since k_2/k_3 was evaluated for each low-pressure run by multiplying the slope of the Q vs. $(I_2)/(HI)$ graph by the value obtained for $k_1K^{\frac{1}{2}}$, it was felt that, for consistency, the value of $k_1.K^{\frac{1}{2}}$ used should be that accepted as the best value, namely, that from the high-pressure runs. The values of k_2/k_3 quoted in Table XI are thus about 10% lower, on the average, than those listed in Table X, since the latter were obtained using the value of $k_1K^{\frac{1}{2}}$ deduced from the same low-pressure run as the slope of the Q vs. $(I_2)/(HI)$ graph.

FIG. 18.

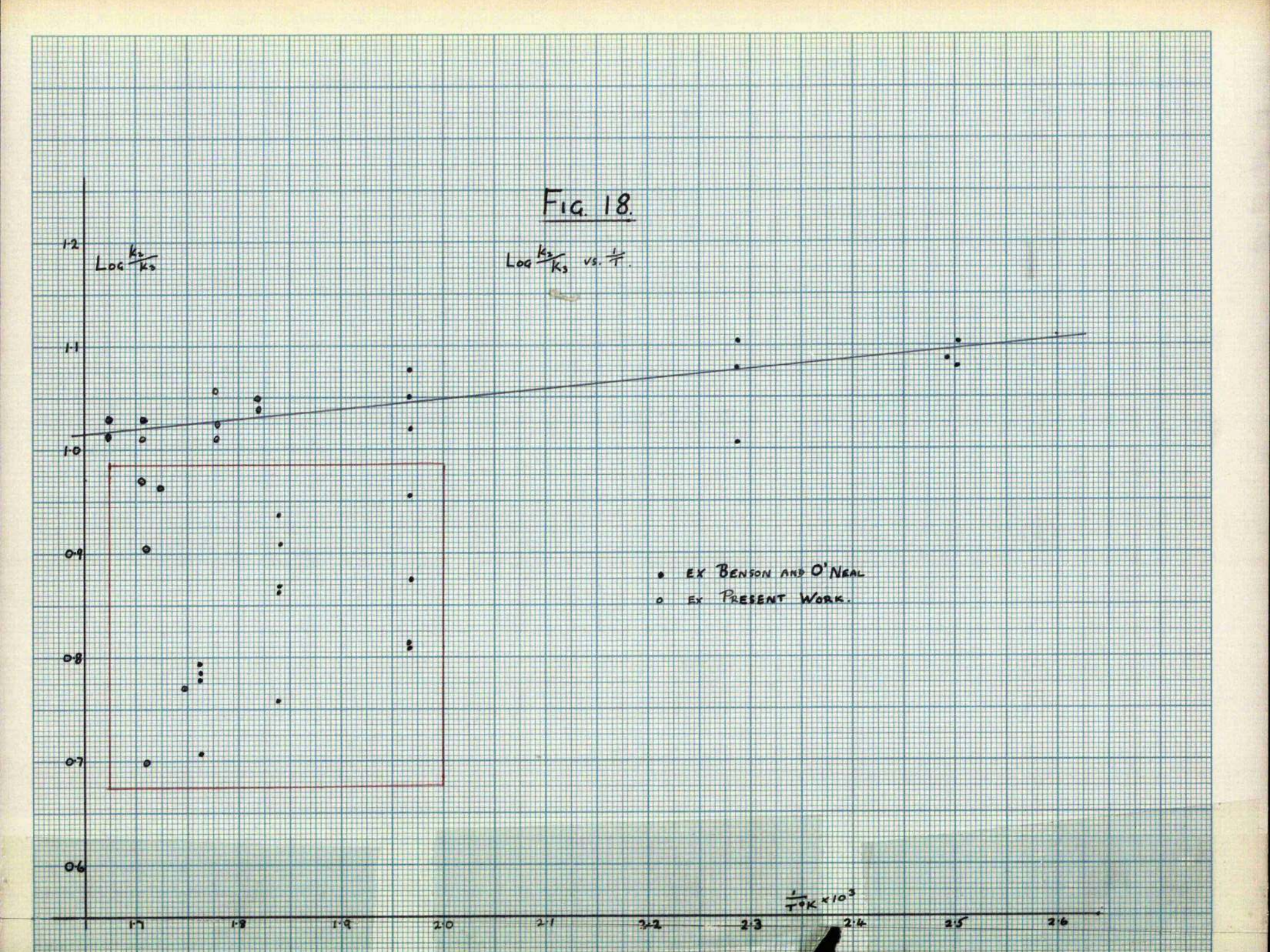

Log $\frac{k_2}{k_3}$ vs. $\frac{1}{T}$.
Log $\frac{k_2}{k_3}$
1·2
1·1
1·0
0·9
0·8
0·7
0·6
• EX BENSON AND O'NEAL
o EX PRESENT WORK.
$\frac{1}{T°K} \times 10^3$
1·7
1·8
1·9
2·0
2·1
2·2
2·3
2·4
2·5
2·6

TABLE XI

Values of k_2/k_5

T^oK	k_2/k_5	T^oK	k_2/k_5	T^oK	k_2/k_5
401.5	12.2	508.5	7.5	580	8.0
399.5	12.0	544	8.6	585.5	4.5
"	12.7	"	7.3	585	8.3
457.5	10.1	"	7.4	586	9.5
"	11.9	"	5.7	"	9.3
"	12.7	"	8.1	586.5	8.7
508.5	11.2	567.5	5.1	550	10.1
"	11.9	"	6.2	549.5	9.4
"	10.4	"	6.0	562	9.9
"	9.0	"	6.1	"	9.2
"	6.4	565	10.2	597.5	9.4
"	6.5	572.5	5.4	"	8.7

The first 22 values are those obtained by Benson and O'Neal,[68] the remainder being the result of the present work. The Arrhenius plot is shown in Fig. 18. There is still a very large scatter, the data of Benson and O'Neal following the trend observed in the present work, and it is feasible to assume that a pattern exists among the higher values of log k_2/k_5. If the points encircled by the red line in Fig. 18 are ignored, the points remaining of the combined data

fit a straight line given by

$$k_2/k_3 = (5.5 \pm 0.05) \cdot e^{(680 \pm 50)/RT}$$

This is probably the best value obtainable for k_2/k_3 from present data, but the errors quoted correspond only to the scatter of the chosen points. Indeed, the values of the Arrhenius parameters, although reasonable, may be in considerable error due to our preference for the higher k_2/k_3 values.

It is of interest to note that Benson and O'Neal did not appear to pretreat their reaction vessel in any way, and observed a much larger proportion of "spurious" runs than in the present work. This suggests that the large scatter in the values of k_2/k_3 may be due to a surface effect of some kind. The role of surface effects in the present work is discussed in a later section.

Evaluation of the Carbon-Iodine Bond Dissociation Energy.

The forward and reverse processes of the equilibrium

$$I + CH_3I \rightleftharpoons CH_3 + I_2,$$

are seen to correspond to reactions (1) and (2) respectively. Since the numbers of molecules of products and of reactants are equal, $\Delta H^\circ_{568} = \Delta E^\circ_{568} = E_1 - E_2$, where E_1 and E_2 are the activation energies found for reactions (1) and (2) at 568°K, the mean experimental temperature.

The value of E_1 has been evaluated as 19.2 ± 0.5 k.cals.per mole, but the only available information concerning E_2 is a value of

680 ± 50 cals. per mole for $E_5 - E_2$. In order to estimate a value of E_2, an additional assumption must be made. One well-known relation that could be used is Hirschfelder's Rule,[70] which states that the activation energy for an exothermic metathetical radical reaction is approximately 5.5% of the bond dissociation energy of the bond being broken. This rule, which was based on semi-empirical calculations, is obviously not exactly correct, as the energy of the bond being formed during the reaction would intuitively be expected to affect the energy level of the transition complex. It might thus be expected that a correlation should exist between activation energy and enthalpy for such reactions, and various writers have discussed this suggestion, (see, for example, Semenov[71]).

However, the assumption that E_2 and E_5 correspond to the same fraction of D(I-I) and D(H-I) respectively is probably as valid as any that could be made in the absence of more complete information.

Then, from the equations E_5-E_2 = 700 cals., and E_2/E_5 = 35.5/71, we deduce E_2 = 700 cals., and E_5 = 1400 cals. The error is liable to be considerable, both from the value assumed for E_5-E_2, and from the arbitrary nature of the assumption made regarding E_2/E_5. Thus, the value deduced for E_1-E_2 = 18.5 k.cals. per mole, is probably only reliable to within ± 1 k.cal. per mole.

A further correction of $\frac{1}{2}$ RT must be subtracted from these values of E_1 and E_2, to make some allowance for the temperature-dependence of the A-factors. This type of correction is based on the classical

collision theory of kinetics, and is only an approximation to the true temperature dependence. However, if it is assumed that A_1 and A_2 vary with temperature in the same fashion, these corrections cancel when calculating E_1-E_2.

Thus, $\Delta H^\circ_{568} = E_1 - E_2 = 18.5$ k.cals. per mole, and this quantity is related to $D(CH_3-I)$ by the relation

$\Delta H^\circ = 18.5$ k. cals. per mole $= D(CH_3-I)-D(I-I)$.

From the data of Perlman and Rollefson,[69] $D(I-I)$ at 568°K is calculated to be 56.5 ± 0.1 k. cals. per mole, (see Appendix V), whence $D(CH_3-I)$ is found to be 55.0 k. cals. per mole at 568°K, with an uncertainty of the order $\pm$ 1 k. cal. per mole.

The correction necessary to reduce ΔH°_{568} to ΔH°_o is shown in Appendix VI to be of the order 1.1 k. cals. per mole. If ΔH°_o is thus taken as 17.4 k. cals. per mole, and the value of $D(I-I)$ at 0°K as 35.5 k. cals. per mole; then $D(CH_3-I)$ at 0°K is deduced to be 52.9 k. cals. per mole.

Similarly, the correction $\Delta(H^\circ_{298}-H^\circ_o)$ is found to be 0.7 k. cals. per mole, so that ΔH°_{298} is 18.1 k. cals. per mole. $D(I-I)$ is given by Perlman and Rollefson[69] as 36.1 k. cals. per mole, so that at 298°K, $D(CH_3-I)$ is deduced to be 54.2 k. cals. per mole.

The uncertainty in these values is probably of the order $\pm$ 1 k. cal. per mole. Within these limits, the values obtained are in excellent agreement with the results of other methods, as described in a previous section.

Pre-Exponential Factors.

The A- factor for reaction (1) has been found to be $10^{10.71}$ litres moles^{-1} secs.$^{-1}$ at 568°K. It is of interest to compare this value with those predicted by collision theory and by transition-state theory.

Classical collision theory gives a value for the A-factor of 5.5×10^{13} litres moles^{-1} secs.$^{-1}$, on assuming collision diameters of 5.5 Å and 5.1 Å for an iodine atom and a methyl iodide molecule, respectively. (Appendix VII). The calculation is subject to the usual uncertainties, but gives a P- factor of about 10^{-2}.

The experimental entropy of activation was calculated for 568°K using the formula

$$k_1 = k_B T/h \cdot e^2 \cdot e^{S/R} \cdot e^{-E_1/RT},$$

where k_B is Boltzmann's Constant, h is Planck's Constant, and S is the entropy of activation. The value thus obtained for S was -14.75 cals. moles^{-1} degrees^{-1}, for a standard state of 1 mole per litre. The derivation of the formula and the numerical calculation are described in Appendix VIII.

The "theoretical" entropy of activation was calculated by the methods of statistical mechanics. The transition complex (1) was assumed to be linear, with respect to the carbon and two iodine atoms. The transmission coefficient was assumed to be unity, and free rotation of the methyl group around the C - I - I axis was also assumed. Full details of the calculation are given in Appendix IX, the value obtained

being - 17.49 cals. moles^{-1} degrees^{-1}, again for a standard state of 1 mole per litre.

There is thus a discrepancy of 2.74 entropy units between the experimental and theoretical entropies of activation. This corresponds to a factor of about 5 in the A- factor, and represents reasonable agreement between experiment and theory, as it is generally accepted that the limit of reliability of transition-state calculations of A- factors is of the order of a factor of 10. Thus, the assumption of a universal frequency factor $k_B T/h$ for the decomposition of transition complexes may itself be in error[74] by a factor of about 10.

Having determined A_1, the value of A_2 can be estimated from the relation $\Delta S^{\circ}_{1.2} = R \ln A_1/A_2$, where $\Delta S^{\circ}_{1.2}$ is the entropy change for the equilibrium

$$I + CH_3I \rightleftharpoons CH_3 + I_2$$

A value of 5.5 entropy units has been estimated for this entropy change at 298°K, (see Appendix X). The temperature 298°K was chosen because a reasonably reliable estimate of the entropy of a methyl radical is available at this temperature. If it is assumed that A_1 varies as $T^{\frac{1}{2}}$, then at 298°K, $A_1 = 10^{10.57}$ litres moles^{-1} secs.$^{-1}$ Thus, $\log A_2 = \log A_1 - \Delta S^{\circ}_{1.2}/4.57$, whence $A_2 = 10^{9.57}$ litres moles^{-1} secs.$^{-1}$ at 298°K.

From this value of A_2, and from the value experimentally determined for $A_2/A_5 = 5.3$, $A_5 = 10^{8.65}$ litres moles^{-1} secs.$^{-1}$ at

298°K. The ratio A_2/A_3 should be practically independent of temperature.

Finally, from a consideration of the opposed reactions (3) and (5):

$$CH_3 + HI \underset{(5)}{\overset{(3)}{\rightleftharpoons}} CH_4 + I,$$

A_5 can be estimated from the value derived for A_3 and from the value of $\Delta S^\circ_{3.5}$. This has been estimated as - 8.9 cals. moles^{-1} degrees^{-1}, (see Appendix X), so log A_5 = log A_3 - $\Delta S^\circ_{3.5}/4.57$, whence A_5 = $10^{10.60}$ litres moles^{-1} secs.$^{-1}$ at 298°K.

Summary and Discussion of Rate Parameters evaluated in Present Work.

For convenience, the values of rate parameters derived in the present work are listed in Table XII. Comments on their reliability, and comparisons with other data, are given below.

TABLE XII

Reaction	log A (litres moles^{-1} secs.$^{-1}$)	E(k.cals./mole)	Temp.(°K)
$I + CH_3I \longrightarrow CH_3+I_2$ (1)	10.71	19.2	570
$CH_3+I_2 \longrightarrow CH_3I+I$ (2)	9.37	0.7	298
$CH_3+HI \longrightarrow CH_4+I$ (3)	8.65	1.4	298
$I+CH_4 \longrightarrow CH_3+HI$ (5)	10.74	34.4	570

The values of the parameters for reaction (1) were directly determined experimentally, and appear to be entirely reasonable. The value of E_1 has been shown to lead to a value of $D(CH_3\text{-}I)$ consistent with recent electron-impact and thermochemical data, and the value of A_1 to be in line with theoretical transition-state calculations.

The rate constant for the closely analogous reaction

$$Br + CCl_3Br \longrightarrow CCl_3 + Br_2$$

has been determined by Sullivan and Davidson.[75] The A- factor for this reaction was found to be $10^{10.97}$ litres moles^{-1} secs.$^{-1}$ at 570°K, and this represents reasonable agreement between the A- factors of the two reactions.

The value quoted for E_2, although reasonable, is subject to a fair degree of uncertainty. Thus, the difference $E_5\text{-}E_2$ was determined experimentally from preferred data, and this difference was then split into its component values by a semi-empirical procedure. The value of A_2 was derived from that of A_1, together with an estimate of the entropy change $\Delta S^\circ_{1.2}$, and so is fairly reliable.

E_5 is subject to the same uncertainties as E_2, while A_5 was derived from the value deduced for A_2 and the experimentally determined ratio A_2/A_5. This latter quantity, although reasonable, is subject to the same objections as $E_5\text{-}E_2$.

Reactions (2) and (3) involve the attack of methyl radicals on diatomic molecules, and Table XIII summarises the data available for such reactions.

TABLE XIII

Reaction	Products	E_5-E_2	A_5/A_2	E	log A	Reference
CH_5+HI	CH_4+I	0.7	0.19	1.4	8.65	Present work,
CH_5+I_2	CH_3I+I			0.7	9.57	together with 68
CH_5+HI	CH_4+I	0.75	0.25	1.5	-	15
CH_5+I_2	CH_3I+I			0.75	-	15
CH_5+HBr	CH_4+Br	0.95	0.15	1.55	-	15
CH_5+I_2	CH_3I+I			0.6	-	15
CH_5+HCl	CH_4+Cl *	2.4	0.04	-	-	15
CH_5+I_2	CH_3I+I			-	-	15
CH_5+HCl	CH_4+Cl	-	-	2.5	8.6	89
CH_5+H_2	CH_4+H	-	-	10.0	8.49	90
CH_5+D_2	CH_3D+D	-	-	11.8	8.85	90
CD_5+H_2	CD_3H+H	-	-	11.1	9.05	90
CD_5+D_2	CD_4+D	-	-	10.9	8.49	90

* Authors believe results to be unreliable.

Activation energies are in k. cals. per mole, A-factors in litres moles^{-1} secs.$^{-1}$. E_5-E_2 and A_5/A_2 refer to the ratio k_5/k_2, where reactions (5) and (2) are:

$$CH_5 + HX \longrightarrow CH_4 + X \qquad (5) \quad (X = Br \text{ or } I)$$

$$CH_5 + I_2 \longrightarrow CH_3I + I \qquad (2)$$

The separate values of E_3 and E_2 were derived from the experimentally determined values of E_3-E_2 by assuming that each was the same fraction of the dissociation energy of the bond broken during the reaction, i.e. $E_3/D(H-X) = E_2/D(I-I)$. It is reassuring to note that the value of E_2 derived from the study of the competition for methyl radicals between HBr and I_2 is the same as that derived from the competition between HI and I_2, and that the two independently obtained results for the latter agree. This would indicate that the above assumption concerning E_2/E_3 is valid, albeit arbitrary. This is further confirmed by the fact that the unambiguous activation energy determined for the reaction $CH_3 + HCl \longrightarrow CH_4 + Cl$ is practically the same fraction of D(H-Cl) as the other E/D ratios. These ratios are in the range 1.9% to 2.2%.

The activation energies for the attack of methyl and trideuteromethyl radicals on hydrogen and deuterium molecules do not, however, fall into the above pattern, being larger by almost an order of magnitude. The same trend is also observed in the analogous reactions of hydrogen atoms with diatomic molecules, as shown in Table XIV.

TABLE XIV

Reaction	Products	E	Reference
$H + Br_2$	$HBr + Br$	0.9	91
$H + HBr$	$H_2 + Br$	0.9	91
$H + HCl$	$H_2 + Cl$	4.0	92
$H + HI$	$H_2 + I$	1.4	57
$H + p\text{-}H_2$	$H + o\text{-}H_2$	5.5	93
$H + D_2$	$D + HD$	6.5	93
$D + H_2$	$H + HD$	5.4	93
$D + p\text{-}D_2$	$D + o\text{-}D_2$	6.0	93

In some cases the activation energies of the reverse processes were experimentally determined, and the activation energies quoted in Table XIV were calculated from these together with heats of reaction derived from bond dissociation energies.

Thus, it would appear that in general, the activation energies for the attack of free atoms and radicals on hydrogen or deuterium molecules do not fall into the pattern of activation energies for the attack on halogen or halogen halide molecules. From the results listed in Table XIII, it appears that for the metathetical reactions of methyl radicals with halogen or halogen halide molecules, forming a methyl halide or methane plus a halogen atom, the activation energy is about 2% of the dissociation energy of the bond broken in the reaction.

The A- factor obtained in the present work for the reaction

$$CH_3 + HI \longrightarrow CH_4 + I$$

is seen to agree closely with that determined for the very similar reaction $CH_3 + HCl \longrightarrow CH_4 + Cl$

Since the derivation of the former involved the evaluation of the ratio A_2/A_5, this agreement offers further confirmation of the validity of the assumptions made when treating the relevant data, and the somewhat arbitrary rejection of certain runs. (See Fig. 18).

The value quoted in Table XII for A_5 is the value derived in the previous section for 298°K, corrected to 570°K. It should be noted that errors made in estimating the entropies of CH_3 and I cancel in the sequence leading to a value of A_5, the overall entropy change effectively involved being that for the process $CH_3I + HI \longrightarrow CH_4 + I_2$. Thus, errors in A_5 arise only from entropy values assigned to stable molecules, which should be fairly accurate, and from experimental errors in A_1 and A_2/A_3.

Reaction (5) is analogous to the rate-determining step found by Kistiakowsky and Van Artsdalen[72] for the bromination of methane, i.e.

$$Br + CH_4 \longrightarrow HBr + CH_3$$

$$\text{cf. } I + CH_4 \longrightarrow HI + CH_3 \quad - (5)$$

Theoretical and experimental entropies of activation for reaction (5) were calculated as for reaction (1). (See Appendix XI). For purposes of comparison, the entropies were calculated for a temperature of 570°K and a standard state of 1 mole. per $cm.^3$, as had been done for

the bromine reaction. The values obtained are listed in Table XV, in cals. moles^{-1} degrees^{-1}.

TABLE XV

Reaction	Products	ΔS^* theoretical	ΔS^* experimental	Reference
$I + CH_4$	$HI + CH_3$	-1.5	-0.9	Present work
$Br + CH_4$	$HBr + CH_3$	-1.84	-1.81	72

The theoretical and experimental values quoted by Kistiakowsky and Van Artsdalen are very close, but the significance of this agreement is probably not great.

However, the entropies of activation are of the same order for the two reactions, with a tendency for the iodine atom reaction to have a slightly more positive value. This can be explained from the point of view of collision theory by postulating that the larger iodine atom need not approach a methane molecule along the precise axis of a carbon-hydrogen bond to within the more precise limits applicable for attack by a smaller bromine atom. The former reaction will thus have a higher P- factor than the latter, as observed.

In terms of transition state theory, when the halogen atom and methane molecule coalesce to form the transition complex, the entropy decreases by an amount corresponding to three translational degrees of freedom. This decrease is partially offset by the entropy gained from three additional vibrational degrees of freedom, and from the increase in the rotational contribution caused by the increased moments of inertia. Since the mass of an iodine atom is over 50%

greater than that of a bromine atom, both of these entropy-increasing effects should be larger in the former case, since vibrational frequencies will be lower, and moments of inertia higher, than in the latter case.

The fact that the value of A_5 thus appears to be reasonable offers further justification for the value assigned to A_2/A_3.

The value of E_5, quoted in Table XII, was estimated from the value of E_3, together with the endothermicity of reaction (5). Since the bond dissociation energies of methane and HI are about 104 and 71 k. cals. per mole, respectively, $\Delta H_{5.3} = 33$ k.cals. per mole, and $E_5 = \Delta H_{5.3} + E_3 = 54.4$ k. cals. per mole.

Survey of Literature on Iodide Decompositions in Light of the Present Work.

The pyrolysis of an organic iodide RI, in presence of a large excess of HI, has now been shown, for R = CH_3, CF_3[2] and $C_6H_5.CH_2$[3], to occur by the mechanism:

$$RI \longrightarrow R + I$$

$$I + RI \longrightarrow R + I_2 \qquad (1)$$

$$R + HI \longrightarrow RH + I \qquad (3)$$

$$I + I \rightleftharpoons I_2$$

The reverse processes of reactions (1) and (3) are effectively prevented by the large excess of HI, while it is possible to study the reaction under conditions such that the rate of the unimolecular fission process is negligible.

The analogous reaction $2HI \longrightarrow H_2 + I_2$ has been shown to proceed partially by a similar atomic mechanism,[57] although the bimolecular step also plays an important role in this case.

It thus seems probable that all organic iodides should decompose according to an essentially similar kinetic scheme. Benzyl iodide contains the weakest carbon-iodine bond of any reasonably common organic iodide, while methyl iodide has probably one of the strongest. (The corresponding bonds in phenyl and vinyl iodides are quoted[45] as having dissociation energies only about 3 to 4 k. cals. per mole higher than that of methyl iodide). Thus, from the point of view of endothermicities, the above mechanism appears to be of general

application, and this is supported by the fact that many of the rate expressions found to describe the pyrolyses of the iodides investigated involve a factor $(I_2)^{\frac{1}{2}}$. If this suggestion is in fact valid, the catalytic action of the iodine atoms has been masked in previous investigations by the simultaneous inhibition due to the iodine molecules. The use of a large excess of HI as a radical catcher removes the complication of secondary reactions of the free radicals, and in particular the inhibitory reaction (2). This blanking out of the inhibitory effect of iodine molecules makes it possible to isolate and measure the catalytic action of the atoms. This general technique would thus appear to offer a general method for the determination of carbon-iodine bond dissociation energies.

The main disadvantage of the method at the moment is the lack of knowledge regarding E_2, the activation energy for the back reaction

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (2)$$

The difficulties have been fully discussed in previous sections. While it would appear that the value of E_2 derived in the present work is reasonable, and probably not in great error, this value was derived by making some more or less arbitrary assumptions. An unambiguous determination of E_2 would thus be of great advantage, the difficulty being that E_2 is so small that errors are liable to be at least as great as the true value of E_2.

Considerations on Transition-state Configurations.

The probability of occurrence of the four-centre transition

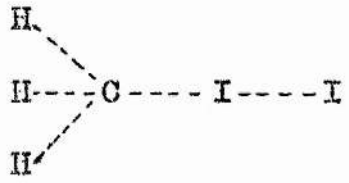
complex involved in reaction(4),

$$CH_3I + HI \longrightarrow CH_4 + I_2 \qquad (4)$$

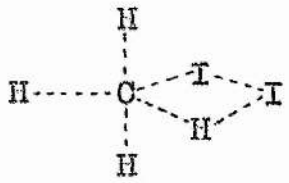
relative to that of reaction (1),

$$I + CH_3I \longrightarrow CH_3 + I_2 \qquad (1)$$

can be considered from theoretical ideas. The two complexes would probably have the forms shown:



(1)



(4)

The four-centre complex (4) involves five atoms bonded to the central carbon, which must therefore hybridise enough orbitals to overlap with the orbitals of the peripheral atoms. The five lowest orbitals available are the 2s, $2p_x$, $2p_y$, $2p_z$, and 3s. The 5s energy level is considerably higher than those associated with principal quantum number 2, and the promotion and hybridisation energies required would be considerable. The analogous reaction

$$2HI \longrightarrow H_2 + I_2$$

has been shown by Sullivan[37] to have an activation energy of about 45.5 k. cals. per mole, of which only about 4.5 k.cals. are due to the endothermicity.

No such difficulties arise in the case of the transition complex for reaction (1). The central iodine atom readily forms molecules analogous to this complex, e.g. the linear ion I_3^-, although, of course the bonds of the transition complex are electron-deficient.

Steric considerations also favour the formation of complex (1) rather than of (4). Carbon, being an element of the first row of the Periodic Table, is a small atom, with not much space around it to accommodate five directly bonded atoms. It is, in fact, a general rule, that elements of the first row have a covalency maximum of four, though extrapolation of this rule concerning stable entities to the case of a transient intermediate may not be valid. However, the entropy of activation for reaction (4) would be very large and negative, due to the high degree of organisation of the transition complex.

On the other hand, the central iodine atom of complex (1) is relatively very large, and has only to accommodate two atoms directly attached to it.

Reference to a transition complex very similar to that suggested for reaction (4) is found in the paper by Schmied and Fink[65] on the isotopic exchange of iodine with methyl iodide. Under certain experimental conditions, the rate of exchange R was given by the expression

$$R = (CH_3I)(I_2) \times 2.5 \times 10^6 \times e^{-9000/RT} \text{ moles cms}^{-3} \text{ secs.}^{-1}$$

This was interpreted as implying that the exchange proceeded via a four-centre complex $CH_3I - I_2$, analogous to the $CH_3I - HI$ complex postulated for reaction (4). This suggestion was supported by the fact that a methyl iodide-iodine complex had previously been shown to exist in n-heptane solution.[64] Schmied and Fink investigated

the temperature dependence of the equilibrium constant $(CH_3I - I_2)/(CH_3I)(I_2)$ in n-heptane solution, over the range 5 to 45°C, using a spectrophotometric method. They found ΔH° to be -4.5 k.cals. per mole, and ΔS° to be -25.8 cals. degrees^{-1} moles,$^{-1}$ for a standard state of 1 mole per litre.

If the entity investigated in solution was in fact the four-centre complex analogous to the transition complex (4), and if the route suggested for the isotopic exchange is in fact the correct one, then the arguments given above, concerning the improbability of occurrence of the complex (4), are suspect. Since the formation of the $CH_3I - I_2$ complex in solution was in fact found to be exothermic, and the activation energy of the exchange reaction only 9 k. cals. per mole, this would strongly suggest that, arguing by analogy, reaction (4) does in fact contribute to the methyl iodide -HI reaction rate. The non-dependence of the rate on HI concentration would have to be explained by some complicated kinetic mechanism.

Fortunately, it seems likely that the entity found to exist in the inert solvent is not in fact the four-centre complex, but is rather a charge-transfer complex. Iodine readily acts as an electron acceptor in this connection, and information regarding these complexes has been given by Murrell.[65] For a series of electron donors and the same acceptor, there is a reasonable linear correlation between the ionisation potential of the donor and the frequency of the charge-transfer band. Murrell shows a plot of these quantities for various

electron donors, with iodine as acceptor, in his review. The ionisation potential of methyl iodide is 9.6 e.V.,[66] and the band observed by Schmied and Fink was in the spectral region 280 mμ. On converting units and plotting on Murrell's graph, the point corresponding to the $CH_3I - I_2$ complex falls on the straight line drawn, to well within the scatter of the rest of the data.

The suggestion that this $CH_3I - I_2$ complex is in fact a charge-transfer complex, is supported by certain observations made by Schmied and Fink. On increasing the concentration of methyl iodide in the solution, with constant iodine concentration, not only did the intensity of absorption increase, but also the wavelength of the band, corresponding to the complex, increased. The energy of the charge-transfer state relative to that of the ground state is given by I - E - C approximately, where I is the ionisation potential of the donor, E the electron affinity of the acceptor, and C a term corresponding to stabilisation of the ionic complex by solvation. Methyl iodide, being highly polar, will enhance this last effect if present in excess, thus decreasing the energy jump, and shifting the absorption band to a longer wavelength. This is in agreement with the trend observed by Schmied and Fink, and would suggest that the $CH_3I - I_2$ complex investigated is in fact of this nature.

It may be remarked that considerable doubt exists concerning the mechanism of the isotopic exchange reaction between iodine and CH_3I. Schmied and Fink[65] supported their suggestion of a four-centre

transition complex by their studies of the complex in solution, but Clark, Pritchard and Trotman-Dickenson[67] found that the rate was of order 0.5 with respect to iodine, and postulated an atomic mechanism. Both sets of workers found that the rate of exchange was strongly surface-dependent.

Thus, it seems probable that the previous arguments, concerning the improbability of occurrence of complex (4), are not invalidated by the work of Schmied and Fink, and the kinetic mechanism postulated to account for the present experimental data is essentially correct.

Surface Effects.

As stated in a previous section, it was assumed throughout that the reaction was entirely homogeneous in nature. Ogg[1] carried out some experiments in which he varied the surface : volume ratio by a factor of eight, at total pressures of 50 mms., without detecting any variation in the rate.

However, it is certain that the state of the wall of our particular reaction vessel influenced the reaction rate. Reproducible behaviour could only be obtained after allowing the reaction vessel to stand with HI in it, for at least an hour, at the operating temperature. The normal practice adopted was to leave it overnight. Presumably the HI had some kind of seasoning effect on the walls of the vessel.

If air was admitted to such a hot, seasoned reaction vessel,

previously pumped out hard with liquid air on traps 1 and 2, a strange effect was noted. The photometer began to record signals indicating the presence of iodine. After a maximum reading was attained, which according to the calibration usually corresponded to about 80 x 10^{-6} moles of iodine, the photometer readings began to fall off, approaching an equilibrium reading asymptotically, this reading corresponding to about 20 x 10^{-6} moles of iodine. On pumping out the air, and comparing the two light intensities reaching the photocells, photocell 1 was found to be recording a greater light intensity, indicating that the transmitting power of the optical cell had been increased in some way.

If a series of three experiments was carried out in this way, without re-seasoning the reaction vessel, the effect observed, while following the same trend qualitatively, diminished in extent with each injection of air. The third injection had only a very small effect.

If HI was then allowed into the reaction vessel in this condition, very similar behaviour was observed, with the difference that, on pumping out the reaction vessel, the transmitting power of the optical cell was found to be less than before the injection. This effect, on successive injections of HI, also diminished, the fourth injection having practically no effect. A very small amount of iodine, about 10^{-5} moles, was collected in the traps on pumping out the first injection.

One other test was applied. Air was allowed into the hot,

seasoned reaction vessel, and left for six hours. The air was then pumped out, and the unbalanced light intensities were not readjusted. HI was then admitted to the reaction vessel, and after five hours, pumped out. It was found that the light intensities, as measured by the photocells, were then balanced to within 2% of I_o. These observations might be explained if the glass reacted with the HI to form iodides, which were decomposed by oxygen with evolution of iodine. We cannot identify the unknown reactant, and apart from noticing this fact, there appears to be little to be gained by further discussion. It would be interesting to have a fused silica bulb and cell, however, in order to repeat these experiments. If no effect was observed, it would suggest that the metallic constituents of the glass play a part.

The evidence quoted in the literature concerning the heterogeneous activity of HI is wide and contradictory,[57;58,59,40]. Schmied and Fink[63] investigated the thermal exchange of iodine with CH_3I and with HI, using I^{151}. For the case of methyl iodide in quartz vessels, the exchange proceeded by two simultaneous routes, one of which was prevented by preheating the reaction vessel overnight at 550°C. The corresponding exchange of iodine with HI was found to be too fast to follow, even at room temperature with the iodine frozen on to the surface.

The experimental technique used in the present investigation did not lend itself to studying the effect of varying the surface: volume ratio of the reaction vessel, as any such variations would have to be

made in the main body of the vessel, while the reaction was followed by observing the optical cell.

Thus, a discussion of possible heterogeneous reactions during the present investigation must rest on indirect evidence. The only direct evidence of surface activity was afforded by the series of experiments described, on the injection of air and of III into the reaction vessel.

Two independent methods were used to evaluate the composite rate constant $k_1 K^{\frac{1}{2}}$. The high-pressure method gave a value about 10% lower than the low-pressure method, the discrepancy being associated with the A- factor. Any surface effect would be expected to make a relatively larger contribution in a low-pressure system than at high pressures, and it is possible that this is the cause of the difference observed. However, a discrepancy of this type is fairly common between values of an A- factor determined by independent methods, and the 10% increase may only represent experimental faults.

Another trend which may be interpreted as a manifestation of surface activity is the strange scatter of values observed for the ratio k_2/k_5 (See Figs. 16 and 18). If it is accepted that the points arbitrarily ignored while drawing Arrhenius plots for k_2/k_5 represent runs during which the surface was for some reason active, thus artificially reducing the effective value of k_2/k_5 in some way, then the Arrhenius equation derived for k_2/k_5 is probably valid. Why the surface should have been active in some cases, and not in others,

when the pretreatment of the reaction vessel was uniform so far as is known, remains a mystery.

The surface effect must have been such as to leave the rate of reaction (1) unaffected, since the values of $k_1K^{\frac{1}{2}}$ found for the "spurious" runs all fell into the general pattern. This implies that reaction (2), the reverse of reaction (1), must also have been unaffected, since the equilibrium position is unambiguously defined by the free energy difference between the two sides of the equilibrium equation. Thus, any catalytic effect of the wall on reaction (2) must have also been exerted on reaction (1), and since the latter was not observed, the low values of k_2/k_3 were not caused by a depression of the rate of reaction (2).

Similarly, any additional reaction postulated to account for the apparent decrease in rate of reaction (2) would automatically cause an apparent increase in the rate of reaction (1). For example, an active surface may facilitate the unimolecular split of CH_3I to $CH_3 + I$, or possibly to $CH_3^+ + I^-$.[68] Since, however, the rate of reaction (1) was not altered by the spurious effect, and since it is difficult to see how such a unimolecular split could depress the apparent rate of (2) without simultaneously raising that of (1), the evidence tends to point against this suggestion.

The value determined for k_2/k_3 could also be made to decrease by an effect which increased the apparent rate of reaction (3). Any effect which removed methyl radicals from the system, so that the back

reaction (2) was rendered less probable, would do this. Such a wall reaction would almost certainly give rise to hydrocarbon products other than methane, such as ethane or ethylene. A complete analysis of trace reaction products would help to decide the question of whether or not any such effect does occur. Benson and O'Neal,[68] in their investigation of the photolysis of acetone in presence of HI, observed a scatter of data very similar to that obtained in the present work, and could detect no ethane in the products. However, more complete data would be required for any fuller discussion.

Reaction of Methyl Bromide with HBr.

It seemed possible that a reaction system consisting of methyl bromide with a very large excess of HBr would show characteristics similar to those described for the analogous CH_3I + HI system. It was hoped that the general method might thus be extended to include the determination of carbon-bromine bond dissociation energies.

The effective mechanism would be, on this theory, as follows:

$$Br + CH_3Br \longrightarrow CH_5 + Br_2 \quad (1)$$

$$CH_5 + HBr \longrightarrow CH_4 + Br \quad (5)$$

$$Br + Br \rightleftharpoons Br_2$$

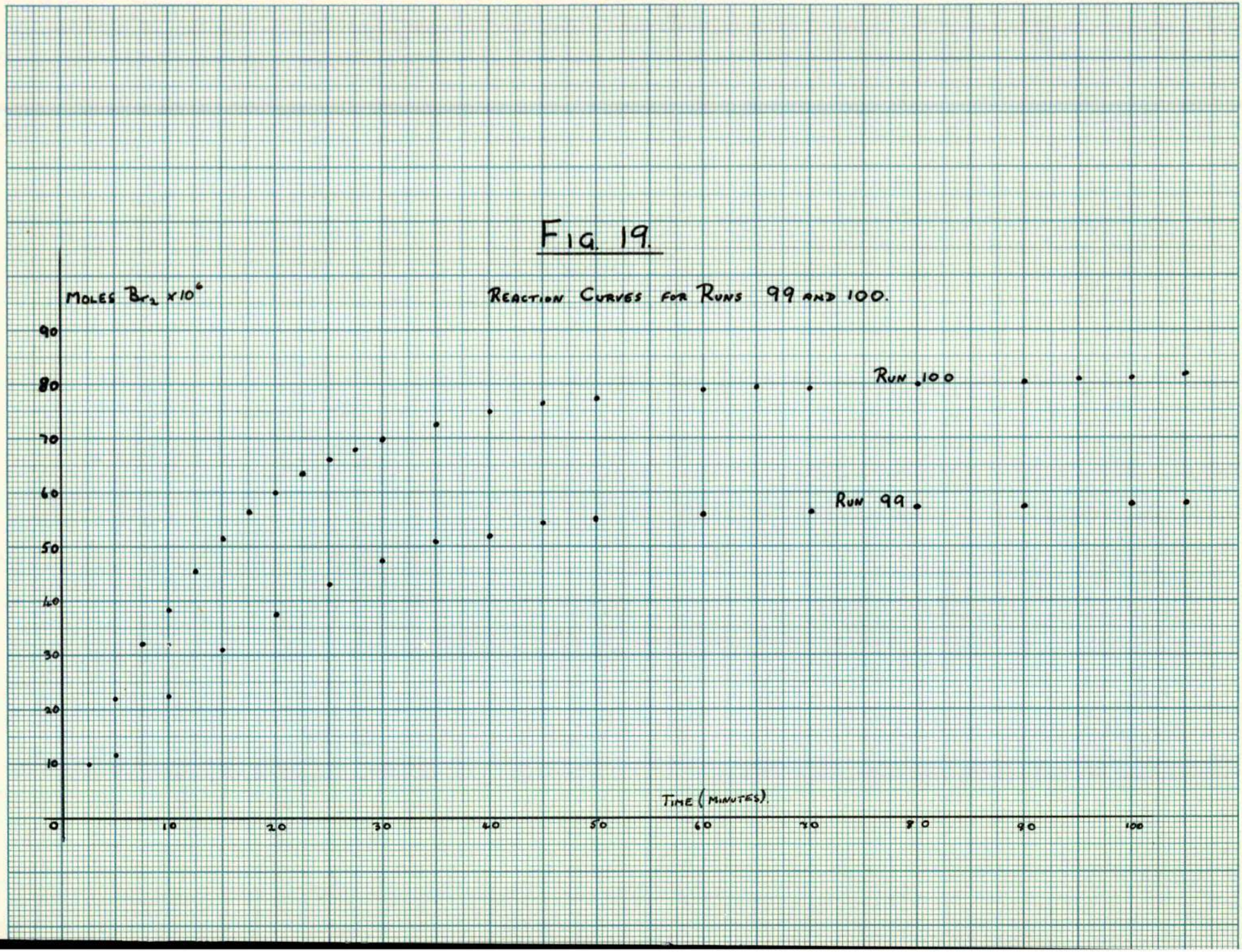
The back reactions

$$CH_5 + Br_2 \longrightarrow CH_3Br + Br \quad (2)$$

and $$Br + CH_4 \longrightarrow HBr + CH_5 \quad (5)$$

would be cut out by the large excess of HBr, as would reaction (6),

Fig. 19.


Reaction Curves for Runs 99 and 100.
Moles Br_2 x 10^6
90
80
70
60
50
40
30
20
10
0
Run 100
Run 99
Time (minutes).
0
10
20
30
40
50
60
70
80
90
100

$$Br + CH_3Br \longrightarrow HBr + CH_2Br \quad (6),$$

which has an endothermicity of only about 15 k. cals. per mole.

Two rather rough runs were carried out to test this suggestion. Air was admitted to the hot reaction vessel for twelve hours, which was then seasoned with HBr for 56 hours before Run 99 was started. No calibration of the photometer for bromine was carried out, apart from the final titrimetric estimations of bromine at the end of the two runs. The photometric system was assumed to obey Beer's Law, as found by previous workers[94] up to 50 mms. of bromine. The relevant data are listed in Table XVI.

TABLE XVI

Run	Initial moles CH_3Br	Initial moles HBr	Final moles Br_2	Temperature ^oK
99	5.245×10^{-4}	1.787×10^{-2}	59.5×10^{-6}	688
100	6.250×10^{-4}	2.566×10^{-2}	82.0×10^{-6}	688

The reaction curves obtained are shown in Fig. 19. Only a few of the determined points are plotted. The type of behaviour is very different from that observed for the CH_3I + HI system, as equilibrium is reached fairly rapidly.

Equilibrium constants $K_c = (Br_2)(CH_4)/(CH_3Br)(HBr)$ were calculated from the data in Table XVI and the assumed overall stoichiometry. The values obtained were 0.70×10^{-3} and 0.52×10^{-5}, giving an average of 0.6×10^{-5}.

Then, the value of ΔF^o_{700} for the overall reaction

$$CH_3Br + HBr \longrightarrow CH_4 + Br_2$$

is given by $\Delta F^\circ_{700} = -RT\ln K_p = -RT\ln K_c = 10.5$ k. cals. per mole. An estimate of ΔS°_{700} can be obtained from published data. For HBr and Br_2, the values of S°_{700} are 53.5 and 66.2 respectively,[78] that for CH_3Br is 69.9,[95] while that for methane is 53.6,[79] all in cals. moles^{-1} degrees.$^{-1}$ All the entropy values quoted are for a standard state of 1 atmosphere pressure, but since the numbers of molecules on the two sides are the same, $\Delta S^\circ_c = \Delta S^\circ_p$ for the equilibrium. Thus, $\Delta S^\circ_{700} = -5.6$ cals. moles^{-1} degrees^{-1} so that $\Delta H^\circ_{700} = \Delta F^\circ_{700} + T.\ \Delta S^\circ_{700} = 7.8$ k. cals. per mole.

Now, ΔH° for the reaction is also given by

$\Delta H^\circ = D(CH_3\text{-}Br) + D(H\text{-}Br) - D(CH_3\text{-}H) - D(Br\text{-}Br)$.

Reliable values for the last three quantities at 0°K are quoted[45] as 86.5, 101, and 45.5 k. cals. per mole respectively. If it is assumed that $\Delta H^\circ_o = \Delta H^\circ_{700}$, which will not be far out as $\Delta(\Sigma C_p)$ is expected to be small, then $D(CH_3\text{-}Br)$ is found to be 67.8 k. cals. per mole at 0°K. This is in remarkable, agreement with the quoted[43] value of 68 k. cals. per mole.

An insight into the reasons for the behaviour of the CH_3Br-HBr system, as compared to that of the CH_3I-HI system, can be gained from a slightly different viewpoint from the purely thermodynamic one discussed above. If the kinetic scheme is given by reactions (1), (2), (3) and (5), together with the bromine equilibrium, the forward and reverse rates are readily shown to be given by:

$$R_f = \frac{d(Br_2)}{dt} = \frac{k_1 K^{\frac{1}{2}} (Br_2)^{\frac{1}{2}}(CH_3Br)k_3(HBr)}{k_5(HBr) + k_2(Br_2)}$$

$$R_r = \frac{d(HBr)}{dt} = \frac{k_5 K^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}(CH_4)k_2(Br_2)}{k_5(HBr) + k_2(Br_2)}$$

At equilibrium, $R_f = R_r$, so that

$$\frac{k_1(CH_3Br)k_3(HBr)}{k_5(CH_4)k_2(Br_2)} = 1, \text{ and } \frac{(CH_3Br)(HBr)}{(CH_4)(Br_2)} = K_c = \frac{k_1k_3}{k_2k_5}$$

Values were assigned to the A- factors by analogy with those found for the iodine system, and activation energies were also estimated by analogy, the endothermicities being calculated from bond dissociation energies.[45] In this way, the following values were assigned:

$$k_5 = 10^{10.6} . e^{-16,000/RT}; \quad k_1 = 10^{10.7} . e^{-23,500/RT};$$

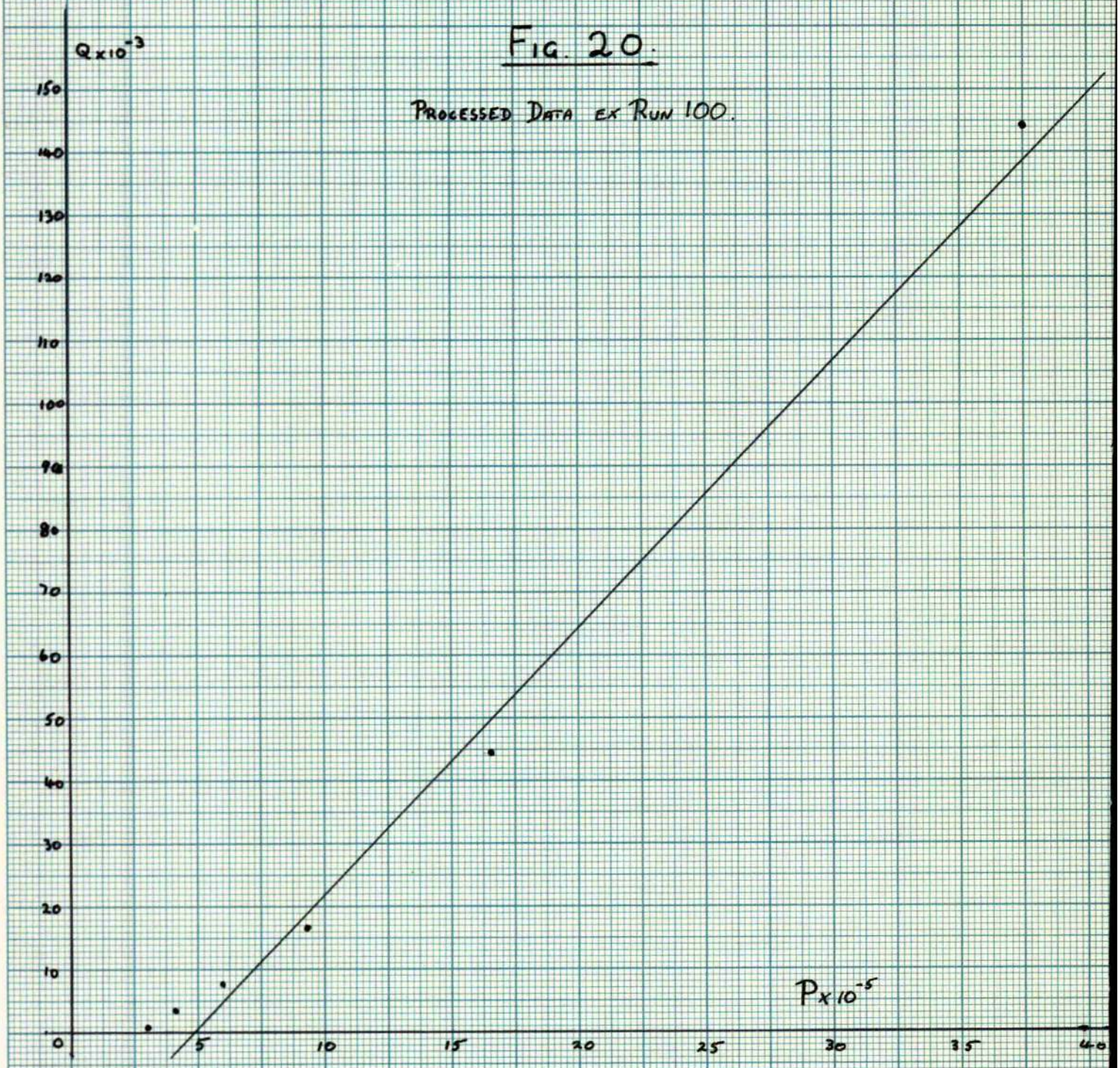
$$k_2 = 10^{8.7} . e^{-1,000/RT}; \quad k_3 = 10^{9.4} . e^{-1,500/RT}$$

The value of log K_c derived from these estimates is -5.5, so that $K_c = 0.5 \times 10^{-5}$, in good agreement with the experimental values.

Thus, the equilibrium position found experimentally for the system $CH_3Br + HBr \rightleftharpoons CH_4 + Br_2$ agrees with that predicted by reliable thermodynamic data, and ideas, derived from the present work on iodides, regarding elementary rate parameters and reaction mechanisms, also tie in with the experimental findings. The main reason for the difference in behaviour between the two reaction systems is seen to lie in the values of E_5, these

FIG. 20.

PROCESSED DATA EX RUN 100.



being of the order 16 and 52 k. cals. per mole for the bromine and iodine systems respectively.

Kinetic analysis of the early portion of Run 100 was attempted on the following lines:

$$R = \frac{d(Br_2)}{dt} = R_f - R_r = \frac{K^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}}{k_2(Br_2)+k_5(HBr)}\left[k_1(CH_3Br)k_3(HBr)-k_5(CH_4)k_2(Br_2)\right]$$

Putting $(CH_4)=(Br_2)$, dividing above and below by $k_5(HBr)$, gives

$$R(1+k_2(Br_2)/k_5(HBr)\ ) = K^{\frac{1}{2}}(Br_2)^{\frac{1}{2}}\left[k_1(CH_3Br)-k_5k_2/k_5(HBr).\ (Br_2)^2\right]$$

Dividing through by $(Br_2)^{5/2}$ gives

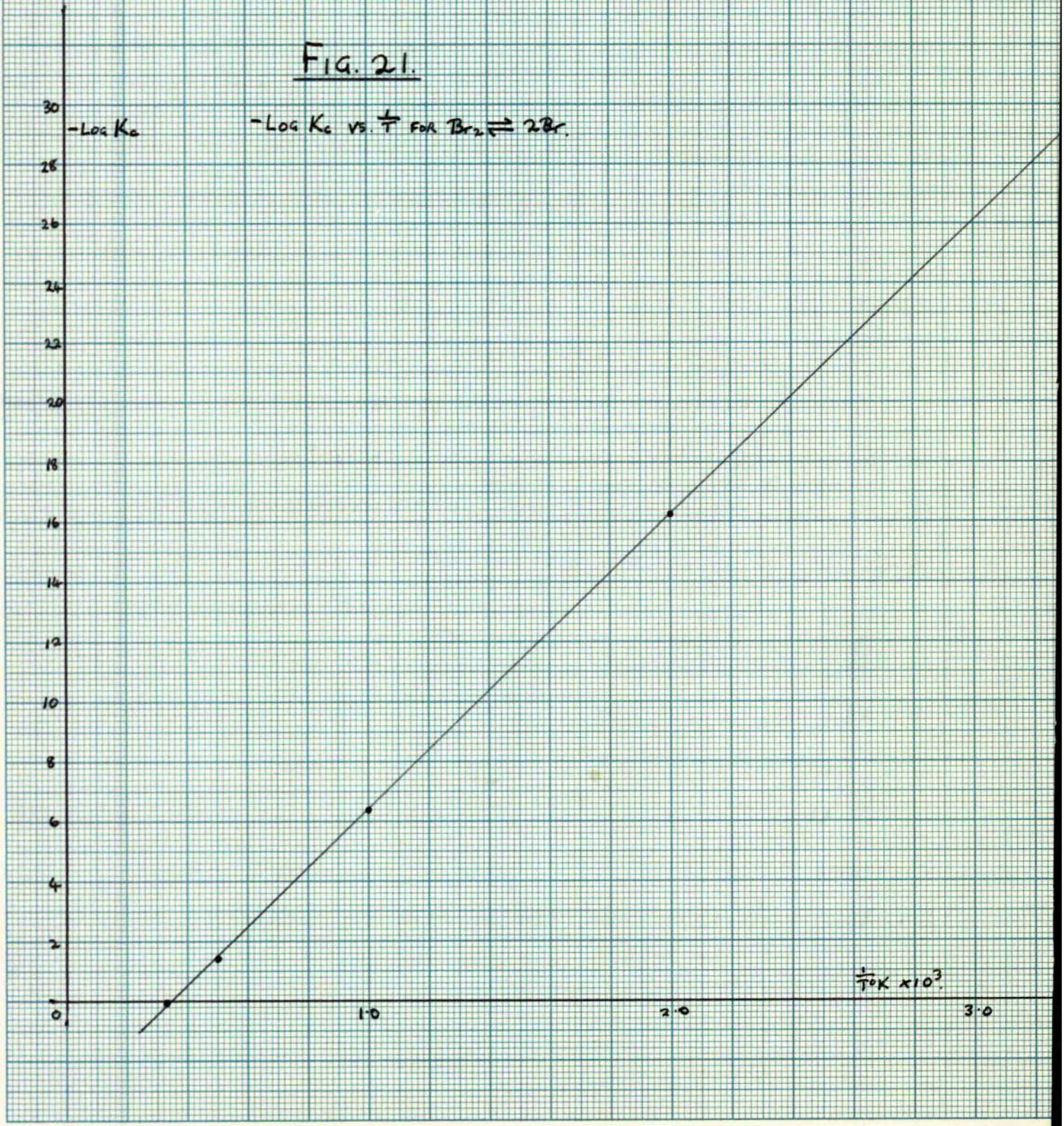
$$\frac{R}{(Br_2)^{5/2}}\left[1+\left(\frac{k_2(Br_2)}{k_5(HBr)}\right)\right] = \frac{k_1K^{\frac{1}{2}}.(CH_3Br)}{(Br_2)^2} - \frac{k_5k_2K^{\frac{1}{2}}}{k_5(HBr)}$$

If (HBr) is assumed constant, and if $k_5(HBr) \gg k_2(Br_2)$ so that $1 + \left[k_2(Br_2)/k_5(HBr)\right] \doteqdot 1$, a plot of $R/(Br_2)^{5/2}$ against $(CH_3Br)/(Br_2)^2$ should give a straight line of slope $k_1K^{\frac{1}{2}}$.

The two functions were calculated for Run 100, the values of R being obtained from the slope of the reaction curve, (Fig. 19) and the plot is shown as Fig. 20. It has a definite curvature, in the direction predicted by assuming that $1 + k_2\ (Br_2)/k_5(HI)$ becomes appreciably greater than unity as reaction proceeds. (Traversing Fig. 21 from top right to bottom left corresponds to the forward reaction direction).

However, the slope of the best straight line gives $k_1K^{\frac{1}{2}} = 4 \times 10^{-2}$ litres$^{\frac{1}{2}}$ moles$^{-\frac{1}{2}}$ secs.$^{-1}$ A value of $K^{\frac{1}{2}}$ can be obtained from

FIG. 21.

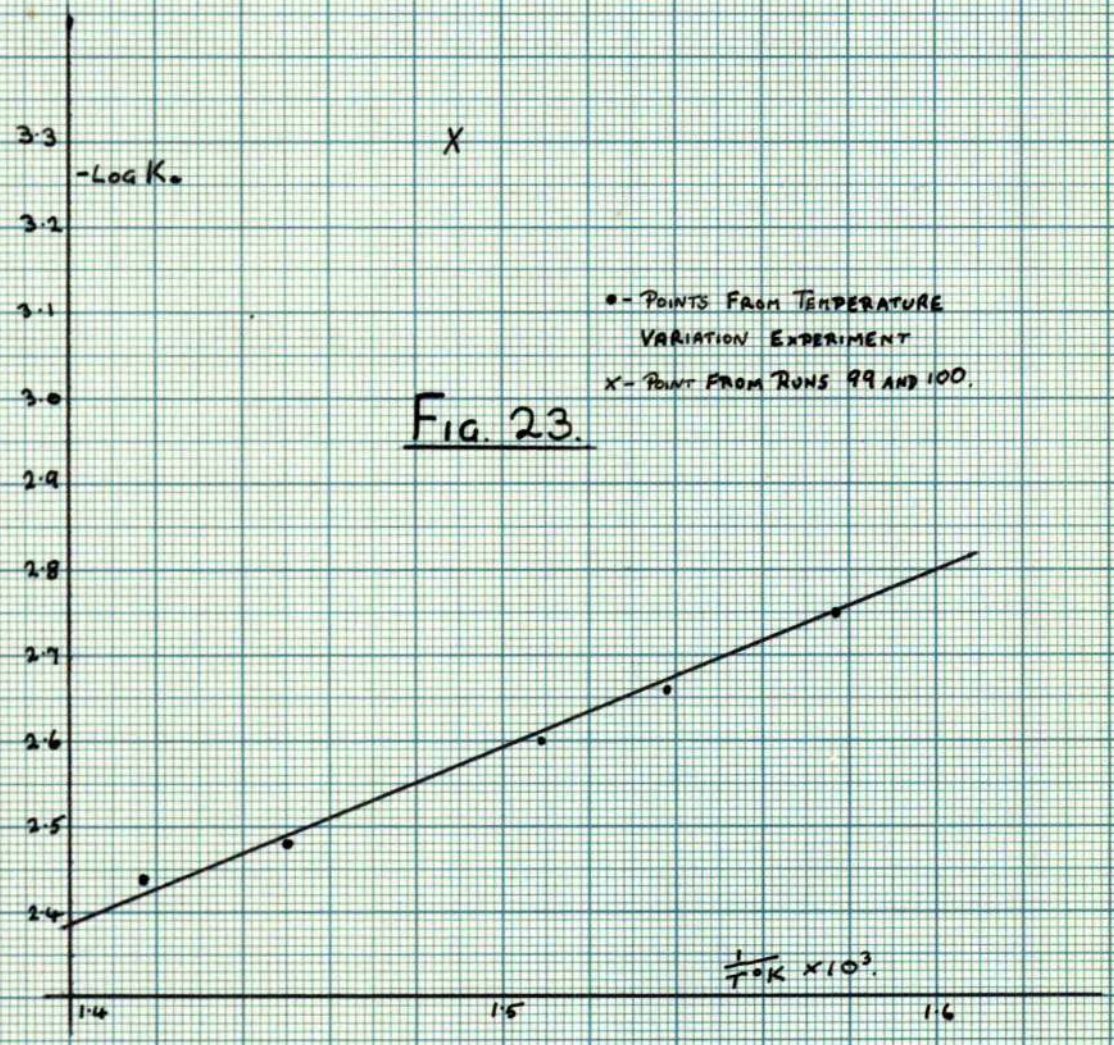

-Log Kc vs. 1/T for Br2 ⇌ 2Br.
-Log Kc
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
1·0
2·0
3·0
1/T°K x10³.

the data of Butkow.[96] A plot of log K_c against $\frac{1}{T}$ is shown as Fig. 21, from which $K_{688} = 10^{-10.8}$ moles litres^{-1}. Then, $k_1 = 4 \times 10^{-2}/10^{-5.4} = 1 \times 10^{4}$ litres moles^{-1}secs.$^{-1}$

If the activation energy E_1 is assumed to be the endothermicity plus 1 k. cal. per mole for the reverse reaction, then E_1 = D(CH_3-Br)-D(Br-Br) + 1 = 25.5 k. cals. per mole. On this assumption, log A_1 = 11.5 at 688°K, (A in litres moles^{-1} secs.$^{-1}$), which, assuming a temperature dependence on $T^{\frac{1}{2}}$, gives a value of log A_1 = 11.4 at 570°K. This represents reasonable agreement with the value log A_1 = 10.7 for the analogous iodine reaction, considering that the former value was obtained by making various assumptions about the results of one rather hastily performed experiment.

However, the fact that the value is reasonable gives some indication of the validity of the postulated reaction mechanism, which also receives support from the work of Sullivan and Davidson[73] on the bromination of chloroform, for which they postulated an exactly analogous reaction scheme. It should be noted, however, that reaction (6) has been disregarded, and it seems quite feasible that this step may in fact make a significant contribution, giving rise to CH_2Br_2, and possibly more fully brominated methanes.

In an attempt to clear up this point, it was decided to investigate the equilibrium over a range of temperature. This was done by injecting a run in the usual fashion, with the furnace at a fixed



X

●- Points From Temperature Variation Experiment

X- Point From Runs 99 and 100.

Fig. 23.

temperature. When equilibrium had been reached, as indicated by constancy of the photometer readings, the latter were noted together with the temperature, and the furnace controls were then changed to a higher temperature-setting. This procedure was repeated till a range of 70°K had been covered, when the reaction mixture was frozen out, and its components estimated, in the usual manner.

The various photometer readings were converted to moles of bromine in the reaction vessel on the basis of Beer's Law, and equilibrium constants $Kc = (Br_2)^2/(CH_3Br)(HBr)$ were calculated for each temperature, assuming $(Br_2) = (CH_4)$. The results are summarised in Table XVII.

TABLE XVII

T°K	Moles $Br_2 \times 10^4$	Moles $CH_3Br \times 10^6$	Moles $HBr \times 10^2$	$Kc \times 10^3$
654	1.21	364	2.259	1.79
650	1.52	353	2.258	2.20
662.5	1.39	346	2.257	2.49
689.5	1.56	329	2.255	3.30
705.5	1.62	325	2.255	3.65

Since $d \ln K/dT = \Delta H^\circ/RT^2$, if ΔH° is assumed to be constant over the temperature range investigated, then $\ln K = -\Delta H^\circ/RT + \text{constant}$, so that a plot of log K against 1/T should give a straight line of slope $-\Delta H^\circ/4.57$. This plot is shown in Fig. 23. It is a fairly good straight line, with a slight curvature, given by:

$$-\log K = (1{,}950 \times 1/T) - 0.5$$

The slope gives a value of ΔH°_{700} of + 8.9 k. cals. per mole.

The value of $\Delta (H^{\circ}_{700} - H^{\circ}_{o})$ for the equilibrium can be calculated to be 0.3 k. cals. per mole from published data,[78,79,95] so ΔH°_{o} = +8.6 k.cals. per mole. From quoted values[43] of $D(CH_3-H)$, D(H-Br) and D(Br-Br), this leads to a value of $D(CH_3-Br)$ = 68.6 k. cals. per mole, in good agreement with the accepted value.

However, the equilibrium constant derived from Runs 99 and 100 differs wildly from the trend of this temperature-variation experiment, as shown in Fig. 21. This can be expressed in thermodynamic terms by calculating the entropy change for the equilibrium from the intercept of the log K vs. 1/T plot. This is 0.3 x 4.57 entropy units, = + 1.4 entropy units, which compares badly with the value predicted above of -3.6 entropy units.

This discrepancy in the entropy corresponds to a factor of 10 in the equilibrium constant, and it was suspected that an arithmetical error may have been made in the calculation of the constants, but none could be detected. Another experiment, similar to that just described, was carried out. The behaviour observed was much the same, the values of ΔH°_{o} and ΔS°_{700} derived being 7.8 k. cals. per mole and 1.2 entropy units, respectively.

Thus, the discrepancy between these temperature-variation experiments and Runs 99 and 100 remains unexplained. Lack of time prevented a fuller investigation of the problem, but it is strange that the temperature-variation experiments should have given a good value of ΔH°, while ΔS° was of the wrong sign. It would appear that the

line of work indicated here should be worth following up.

SUMMARY

(1) Methyl iodide was decomposed thermally in a static system, in presence of hydrogen iodide as radical acceptor. The reaction was followed by photometric estimation of the iodine produced, the equipment developed being capable of giving an almost continuous record of iodine concentration, if required.

(ii) At high enough concentrations of hydrogen iodide, the rate became independent of this parameter. Under these conditions, the rate-determining step has been shown to be reaction (1):

$$I + CH_3I \longrightarrow CH_3 + I_2 \qquad (1)$$

Rate constants for this reaction were measured over a range of 74°, in a region where the rate of unimolecular fission is known to be negligible, and the Arrhenius expression for the rate constant found to be $\log k_1 = (10.71 \pm 0.08) - (19{,}200 \pm 200/4.57.T)$, where the A-factor is in litres $moles^{-1}$ $secs.^{-1}$ and the activation energy in cals. $moles^{-1}$.

(iii) Under conditions where the rate was not independent of the HI concentration, the removal of methyl radicals by reaction (5),

$$CH_3 + HI \longrightarrow CH_4 + I \qquad (5)$$

was not complete, so that the back reaction (2),

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (2)$$

played a significant role. The reaction was studied over a temperature range of 48°K under these conditions, and the following

information regarding elementary rate parameters was derived:

$$\log k_1 = (10.78 \pm 0.12) - (19,200 \pm 300)/4.57.T.$$

$$k_2/k_3 = 4.8 \times e^{+\ 910/RT}$$

When the data concerning k_2/k_3 obtained in the present work was combined with that obtained by Benson and O'Neal[68] by an independent method, a temperature range of 198° was covered, and the value derived from the combined data was given by

$$k_2/k_3 = (5.3 \pm 0.05).\ e^{+(680 \pm 50)/RT}$$

(iv) The values determined for activation energies were used to derive a value of the carbon-iodine bonddissociation energy in methyl iodide. The following values, with an uncertainty of about ±1k. cals. per mole, were found:

570°K	-	55.0 k. cals. per mole.
298°K	-	54.2 k. cals. per mole.
0°K	-	52.9 k. cals. per mole.

(v) The pre-exponential factor derived experimentally for reaction (1) has been compared with those predicted on the basis of both collision and transition-state theories of chemical kinetics. The P- factor is of the order of 10^{-2}, while the transition-state prediction agrees with the value observed to within a factor of five.

(vi) Using the values obtained for A_1 and A_2/A_3, and by making estimates of entropy changes, the following values, in litres moles^{-1} secs.$^{-1}$, were obtained for A- factors:

$$A_1 = 10.71 \text{ at } 570^\circ K$$

$A_2 = 9.57$ at 298°K

$A_3 = 8.65$ at 298°K

$A_5 = 10.74$ at 570°K,

where A_5 is the pre-exponential factor for the reaction

$$I + CH_4 \longrightarrow HI + CH_3 \qquad (5)$$

This value of A_5 has been shown to agree both with transition-state predictions, and with the value obtained by Kistiakowsky and Van Artsdalen[72] for the analogous reaction

$$Br + CH_4 \longrightarrow HBr + CH_3$$

(vii) A discussion of possible surface effects has been given, which rests on incomplete evidence, as the photometric method used to follow the reaction did not lend itself to directly testing the homogeneity of the reaction by packing the reaction vessel. However, the particular reaction vessel used was surface-active, and had to be seasoned before reproducible behaviour could be obtained.

(viii) A few exploratory experiments were carried out on the analogous reaction system $CH_3Br + HBr$. The behaviour observed differed from that of the analogous $CH_3I + HI$ system, as the equilibrium position in the former case lies well to the side of the reactants. The equilibrium was investigated over a temperature range of 74°, and equilibrium constants calculated on the assumption that the stoichiometry of the reaction was given by

$$CH_3Br + HBr \rightleftharpoons CH_4 + Br_2$$

ΔH°_{700} was found to be + 8.9 k. cals. per mole, which on correcting

to 0°K, and combining with reliable values of the bond-dissociation energies of the other molecules involved, leads to a value of $D(CH_3\text{-}Br)$ of 68.6 k. cals. per mole, in good agreement with the accepted value.

However, the entropy change derived from the temperature variation experiments differs from that calculated from spectroscopic data by 5 entropy units, and it is possible that the equilibrium is more complicated than assumed above, and that CH_2Br_2 and more fully brominated methanes are also formed.

* * *

APPENDICES

APPENDIX I

Integration of Rate Equation

$$\frac{d(I_2)}{dt} = k_{exp.}(CH_3I)(I_2)^{\frac{1}{2}}$$

Put $(CH_3I)_o = a, (I_2)_o = m$, and let x be the concentration of CH_3I reacted at time t. Since the overall equation is $CH_3I + HI \longrightarrow CH_4 + I_2$, x = concentration of I_2 produced by the reaction at time t, so that $(I_2)t = x + m$.

Then, $\frac{d(x + m)}{dt} = k_{exp.}(a - x).(x + m)^{\frac{1}{2}}$.

$$\text{i.e. } k_{exp.}\, dt = \frac{d(x + m)}{(a - x)(x + m)^{\frac{1}{2}}}$$

Putting $y = x + m$, $d(x + m) = dy$, $(a - x) = (b - y)$, where $b = a + m$, gives $k_{exp.}\, dt = \frac{dy}{(b - y).y^{\frac{1}{2}}}$

Putting $z^2 = y$, $dy = 2z.dz$, so that

$$k_{exp.}\, dt = \frac{2z.dz}{(b-z^2).z} = \frac{2.dz}{b-z^2}$$

$$\text{i.e. } k_{exp.}\, t = 2\int \frac{dz}{(b-z^2)} = 2\int\left[\frac{1/2\sqrt{b}}{\sqrt{b}-z} + \frac{1/2\sqrt{b}}{\sqrt{b}+z}\right] dz$$

$$= \frac{1}{\sqrt{b}}\int\left[\frac{1}{\sqrt{b}-z} + \frac{1}{\sqrt{b}+z}\right] dz$$

$$= \frac{1}{\sqrt{b}} \cdot \ln.\left[\frac{\sqrt{b}+z}{\sqrt{b}-z}\right] = \frac{1}{\sqrt{b}} \ln\left[\frac{1 + z/\sqrt{b}}{1 - z/\sqrt{b}}\right]$$

$$\text{i.e. } k_{exp}t.\sqrt{a + m} = I = \ln.\left[\frac{1 + \sqrt{(x + m)/(a + m)}}{1 - \sqrt{(x + m)/(a + m)}}\right]$$

$$\text{i.e. } e^{I} = \frac{1 + \sqrt{(x + m)/(a + m)}}{1 - (x + m)/(a + m)}$$

$$\text{i.e. } \sqrt{(x + m)/(a + m)} = \frac{e^{I} - 1}{e^{I} + 1} = \tanh I/2,$$

$$\text{since } \tanh x = \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}} = \frac{e^{2x} - 1}{e^{2x} + 1}$$

$$\text{Thus } I/2 = \tanh^{-1} \sqrt{(x + m)/(a + m)}$$

$$\text{i.e. } \tfrac{1}{2}.\ k_{exp.}\ t.\ \sqrt{a + m} = \tanh^{-1} \sqrt{(x + m)/(a + m)} + C.$$

Evaluating C from the condition that $x = o$ when $t = o$, gives

$$t.\ k_{exp.}\ \sqrt{a + m} = 2 \tanh^{-1} \sqrt{(x + m)/(a + m)} - \tanh^{-1} \sqrt{m/(a + m)}$$

APPENDIX II

Volume of Reaction Vessel.

This was determined by filling the reaction vessel with HI, measuring the temperature and pressure, and estimating the HI by titration. Three such experiments gave a value for V of 2.40 ± 0.03 litres.

APPENDIX III

Summarised experimental data for high-pressure runs.

$a = (CH_3I)_o$, $b = (HI)_o$, $m = (I_2)_o$, all in moles litres^{-1}.

V = volume of furnace = 2.40 litres. $(x + m)V$ = amount of iodine in reaction vessel at time t, in moles x 10^6. a.V, m V and b.V in moles x 10^4.

$I/2 = \tanh^{-1} \sqrt{\frac{x + m}{a + m}}$ (see Appendix I).

Run 55. 546°K. a.V = 5.71. b.V = 148. mV = .095. 10/1/62.

t(secs. x 10^{-5})	(x+m).V.	I/2.
1	14.5	.198
2	18.5	.229
3	22.5	.252
4	27	.275
5	31	.299
6	35.5	.320
7	40	.342
8	44.5	.361
9	49.5	.384
10	55	.407
11	61	.431
12	66.5	.455
13	72.5	.476
14	79	.500
15	85	.525
16	91.5	.546

Run 56 $545^{\circ}K$. a.V = 5.81 b.V = 89 m V = 0.11. 11/1/62.

t (secs. x 10^{-5})	(x+m).V.	I/2
1	15	.198
2	19	.225
3	25	.248
4	27.5	.272
5	31.5	.291
6	36	.315
7	40.5	.335
8	45.5	.355
9	50.5	.375
10	55.5	.397
11	60.5	.415
12	66	.436
13	71	.454
14	76.5	.475
15	81.5	.494

Run 57 $540^{\circ}K$. a.V = 5.85 b.V = 142 m V = 0.11. 15/1/62.

t(secs. x 10^{-5})	(x+m)V	I/2
1	14.5	.195
2	17.5	.213
3	20.5	.232
4	23.5	.248
5	26.5	.266
6	29.5	.281
7	32.5	.295
8	36	.312
9	39.5	.327
10	43	.343
11	46.5	.359
12	50.5	.374
13	54.5	.390
14	58	.404

Run 58 557°K a.V = 5.85 b.V. = 156 m V = 0.16. 25/1/62.

t (secs. x 10^{-3})	(x+m)V	I/2
1	19	.222
2	22.5	.242
3	26	.261
4	29	.278
5	32	.291
6	35	.307
8	41	.333
10	47.5	.360
12	54.5	.388
14	61.5	.415
16	68.5	.438
17	72	.454
18	75.5	.466
19	79	.478
20	85	.493

Run 59 532°K. a.V = 5.81 b.V = 149 m V = 0.095. 24/1/62.

t (secs. x 10^{-3})	(x+m)V	I/2
1	10.5	.166
2	12	.178
3	13.5	.189
4	15	.198
6	18	.217
8	21.2	.237
10	25	.259
12	28.5	.278
14	32.5	.298
16	36.5	.317
17	39	.327
18	41	.336
19	43	.346
20	45	.355

Run 60 550.5°K. a.V = 3.81 b.V = 193 m V = 0.19. 25/1/62.

t(secs. x 10^{-3})	(x+m)V	I/2
1	21	.230
2	23	.241
3	25.5	.254
4	28	.269
6	32.5	.293
8	36.5	.312
10	40.5	.330
12	45	.350
14	49.5	.368
16	54	.386
17	56.5	.395
18	59	.404
19	61.5	.415
20	64	.425

Run 61 551.5°K. a.V = 5.84 b.V = 115 m V = 0.05 . 31/1/62.

t(secs. x 10^{-3})	(x+m)V	I/2
2	6	.127
4	18	.142
6	10	.159
8	12	.178
10	15	.197
12	17.5	.215
14	20.5	.234
16	24	.252
18	27	.271
20	30.5	.289
22	34.5	.308

Run 62 551.5°K. a.V = 5.85 b.V = 142 m V = 0.12. 1/2/62.

t(secs. x 10^{-3})	(x+m)V	I/2
2	17	.208
4	21.5	.240
6	26	.261
8	30	.281
10	34	.302
12	38.5	.320
14	42.5	.340
16	47	.359
18	51.5	.379

Run 63 551.5°K. a.V = 5.80 b.V = 154 m V = 0.06. 2/2/62.

t(secs.x 10^{-5})	(x+m)V	I/2
2	7	.135
4	9	.153
6	11	.172
8	15.5	.192
10	16.5	.210
12	19	.228
14	22	.244
16	25.5	.266
18	29.5	.284
20	33.5	.505

Run 64 554°K. a.V = 5.81 b.V = 167. m V = 0.075. 8/2/62.

t(secs. x 10^{-5})	(x+m)V	I/2
2	10	.162
4	13	.184
6	16	.205
8	19	.226
10	22.5	.246
12	26.5	.267
14	31	.288
16	35	.510
18	40	.551

Run 65 560°K. a.V = 5.67 b.V = 166 m V = 0.11 13/2/62.

t(secs. x 10^{-2})	(x+m)V	I/2
5	17	.213
10	22.5	.246
15	28	.281
20	34	.510
25	40	.538
30	46	.565
35	52	.590
40	58.5	.417
45	65.5	.445
50	72.5	.468
55	79.5	.495
60	94.5	.550
65	94.5	.550
70	102.5	.578

Run 66 568.5°K. a.V = 3.65 b.v = 112 m V = 0.13. 14/2/62.

t (minutes)	(x+m)V	I/2
5	18	.225
10	25	.250
15	29	.284
20	34.5	.315
30	46	.364
40	59	.420
50	72.5	.469
60	85.5	.519
65	92	.542
70	99.5	.570
75	106	.594
80	112.5	.615
85	119	.638

Run 67 577°K. a.V = 3.60 b.V = 121 m V = 0.075 15/2/62.

t (minutes)	(x+m)V	I/2
5	17.5	.230
10	27	.277
15	34.5	.317
20	44	.361
25	53.5	.403
30	63.5	.445
35	73.5	.482
40	84	.521
45	94.5	.559
50	104.5	.596
55	115	.635
60	126	.672
65	136.5	.709

Run 68 585.5°K. a.V = 3.45 b.V = 105 m V = 0.10 16/2/62.

t (minutes)	(x+m)V	I/2
5	22	.253
10	36.5	.328
15	50	.398
20	65	.459
25	81	.521
30	97	.582
35	115.5	.645
40	129	.700
45	144	.758

Run 69 588.5°K. a.V = 5.48 b.V = 115 m V = 0.12 17/2/61.

t (minutes)	(x+m)V	I/2
5	26	.276
10	41	.352
15	59	.430
20	78	.498
25	98	.579
30	117	.648
35	136.5	.719
40	156.5	.795

Run 70 595°K. a.V = 5.52 b.V = 99 m V = 0.05 19/2/62.

t (minutes)	(x+m)V	I/2
5	18	.258
7.5	27	.293
10	36.5	.545
12.5	47	.594
15	58	.441
17.5	69	.490
20	81	.539
22.5	93	.589
25	106	.658
27.5	119	.687
30	129	.725
35	151.5	.815
40	171.5	.900

Run 71 596°K. a.V = 5.52 b.V = 192 m V = 0.12 20/2/62.

t (secs. x 10^{-2})	(x+m)V	I/2
1	22	.249
2	30.5	.294
3	40	.345
4	50.5	.392
5	61.5	.458
6	72.5	.481
7	85	.522
8	94	.562
9	104	.600
10	116	.653
11	125	.675
12	136	.713
13	147	.753

Run 72 602.5°K. a.V = 5.50 b.V = 171 m V = 0.04. 26/2/62.

t(secs. x 10^{-2})	(x+m)V	I/2
1	15.5	.235
2	26.5	.292
3	37.5	.348
4	50.5	.410
5	66	.479
6	79.5	.535
7	94	.593
8	108	.648
9	125	.704
10	138	.764
11	155	.824
12	165	.878
13	177	.924
14	189	.978

Run 73 603°K. a.V = 5.45 b.V = 165. m V = 0.02. 27/2/62.

t(secs. x 10^{-2})	(x+m)V	I/2
1	8	.150
2	16	.215
3	26	.280
4	38	.345
5	51.5	.406
6	66	.468
7	82	.531
8	98	.592
9	114	.654
10	130	.712
11	144.5	.768
12	161	.828

Run 74 605°K. a.V = 0 (III blank). b.V = 105 m V = 0.05. 27/2/62.

t(secs x 10^{-2})	(x+m)V
2	5
4	5
6	5
8	5
10	5
12	5
14	5
16	5
18	5
20	5.5
22	5.5

Run 75 605°K. a.V = 3.56 b.V = 88. m V = 0.04 28/2/62.

t(secs. x 10^{-2})	(x+m)V	I/2
1	8	.149
2	15	.208
3	25	.271
4	37.5	.334
5	51	.398
6	65	.454
7	80	.511
8	95	.572
9	110	.630
10	125	.680

Run 76 565°K. Fully reported in text. 5/3/62.

Run 77 560°K. a.V = 3.68 b.V = 87 m V = 0.07 6/3/62.

t(secs. x 10^{-2})	(x+m)V	I/2
1	15	.203
2	25	.252
3	32	.301
4	43	.353
5	54	.399
6	66	.447
7	79	.496
7.5	87	.525

Run 78 565.5°K. a.V = 7.22 b.V = 244. m V = 0.07 7/3/62.

t(secs. x 10^{-2})	(x+m)V	I/2
1	15	.146
2	27.5	.197
3	41.5	.244
4	58.5	.291
5	78	.340
6	99.5	.387
7	122	.435

Run 79 560.5°K. a.V = 11.03 b.V = 206 m V = 0.07 8/3/62.

t(minutes)	(x+m)V	I/2
10	25	.149
20	47.5	.210
30	75.5	.268
40	105	.517
50	137	.368
60	173.5	.418

Run 80 560°K. a.V = 3.70 b.V = 235 m V = 0.16 14/3/62.

t(secs x 10^{-5})	(x+m)V	I/2
1	22.5	.245
2	30.5	.288
3	40.5	.336
4	51.5	.385
5	65	.428
6	75	.473
7	87.5	.518
8	102	.568
9	117	.618
10	132.5	.673

Run 81 560°K. a.V = 3.62 b.V = 296 m V = 0.07 15/3/62.

1	15.5	.195
2	21.5	.246
3	31.5	.301
4	42	.352
5	52.5	.398
6	63.5	.442
7	75.5	.488
8	88.5	.538
9	105	.589

Run 82 560°K. a.V = 3.70 b.V = 205 m V = 0.07 16/3/62.

t(secs. x 10^{-5})	(x+m)V	I/2
1	14	.198
2	22.5	.252
3	31	.289
4	41	.347
5	52	.394
6	64	.445
7	77	.492
8	90.5	.542
9	104	.590
10	118	.640

Run 85 561°K. a.V = 5.60 b.v = 155 m V = 0.04 19/3/62.

t(secs. x 10^{-5})	(x+m)V	I/2
1	9.5	.162
2	16.5	.215
3	25.5	.272
4	35.5	.324
5	46.5	.374
6	59.5	.430
7	72.5	.480
8	86	.532
9	101	.588
10	116	.640

APPENDIX IV

Summarised Experimental data for low pressure runs. a = $(CH_3I)_o$, b = $(HI)_o$, in moles litres^{-1}. M = moles of iodine in reaction vessel at time t, x 10^6. a.V and b.V in moles x 10^6.
$Q = (CH_3I)(I_2)^{\frac{1}{2}} / \frac{d(I_2)}{dt}$, in litres$^{-\frac{1}{2}}$ moles$^{\frac{1}{2}}$ seconds^{-1}.

Run 85 565°K. a.V = 725. b.V = 2580. 9/5/62.

M	t(secs x 10^{-2})	Q x 10^{-2}
25	20	1.04
50	29	1.01
100	44.5	1.32
150	61	1.55
200	79	1.72
250	97	1.81
300	118	2.12
350	142	2.24
400	172	2.81
450	214	

Run 86 572.5°K. a.V = 720 b.V = 3060 15/5/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	8	.52
50	15	.55
100	20.5	.60
150	28	.66
200	35.5	.74
250	45.5	.81
300	52	.86
350	61.5	.88
400	72	.90
450	84	1.05

Run 87 580°K. a.V = 715 b.V = 1620. 17/5/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	7	.36
50	10.5	.37
100	17	.49
150	23.5	.59
200	31	.74
250	39	.84
300	48.5	.95
350	60	1.09
400	74	1.54

Run 88 585.5°K. a.V = 695 b.V = 2655. 24/5/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	4	.26
50	6.5	.23
100	10.3	.29
150	13.8	.32
200	17.8	.35
250	21.8	.39
300	26	.40
350	31	.42
400	36.5	.46
450	45	.50

Run 89 585°K. a.V = 735 b.V = 1960 28/5/62.

M	t(secs x 10^{-2})	Q x 10^{-2}
25	5	.28
50	8	.35
100	12.8	.39
150	17.5	.46
200	22.5	.54
250	28.3	.61
300	35	.66
350	42.8	.77

Run 90 586°K. a.V = 715 b.V = 2050 29/5/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	5	.28
50	8	.30
100	12.5	.37
150	17.5	.45
200	22.5	.48
250	28	.58
300	34.8	.68
350	42.5	.75

Run 91 586°K. a.V = 725 b.V = 2405 30/5/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	4.8	.29
50	7.5	.26
100	12.8	.34
150	16.3	.41
200	21	.45
250	26	.52
300	31.5	.59
350	38.5	.65
375	42.3	.70

Run 92 586.5°K. a.V = 715 b.V = 2330 31/5/62.

M	t(secs x 10^{-2})	Q x 10^{-2}
25	4.5	.25
50	7.5	.27
100	12	.33
150	16	.40
200	20.8	.43
250	25.8	.49
300	31.5	.57
350	38	.64

Run 93 550°K. a.V = 740 b.V = 2470 8/6/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	52	2.01
50	52.5	2.35
75	70	2.50
100	87.5	2.70
150	120.5	3.15
200	156	3.76
250	198	4.50
275	221	4.52
300	246	5.05
325	273	

Run 94 549.5°K a.V = 740 b.V = 2110 9/6/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	40.5	2.06
50	62	2.50
75	80	2.62
100	98	2.81
125	116	3.17
150	135.5	3.56
200	175.5	4.28
225	196	4.37
250	220	4.76
275	246	

Run 95 562°K a.V = 725 b.V = 2515 14/6/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	18	1.08
50	28.5	1.10
75	37.5	1.21
100	46	1.51
150	63.5	1.52
200	82.5	1.86
250	103.5	2.12
300	127.5	2.23
325	140.5	2.55
350	155.5	

Run 96 562°K. a.V = 725 b.V = 2080 16/6/62.

M	t(secs. x 10^{-2})	Q x 10^{-2}
25	18.5	1.04
50	29	1.08
75	38.5	1.21
100	47	1.42
150	65	1.66
200	85	1.95
225	95.5	2.05
250	106	2.20
275	118	

Run 97 Fully reported in text. 26/6/62.

Run 98 597.5°K. a.V = 715 b.V = 1990 29/6/62.

M	t(mimutes)	Q x 10^{-2}
25	5.75	.138
50	6.25	.153
75	8.25	.161
100	10	.175
150	14.25	.224
200	18.5	.258
250	25.5	.505
275	26.25	.516
300	29.0	.553
525	32.5	

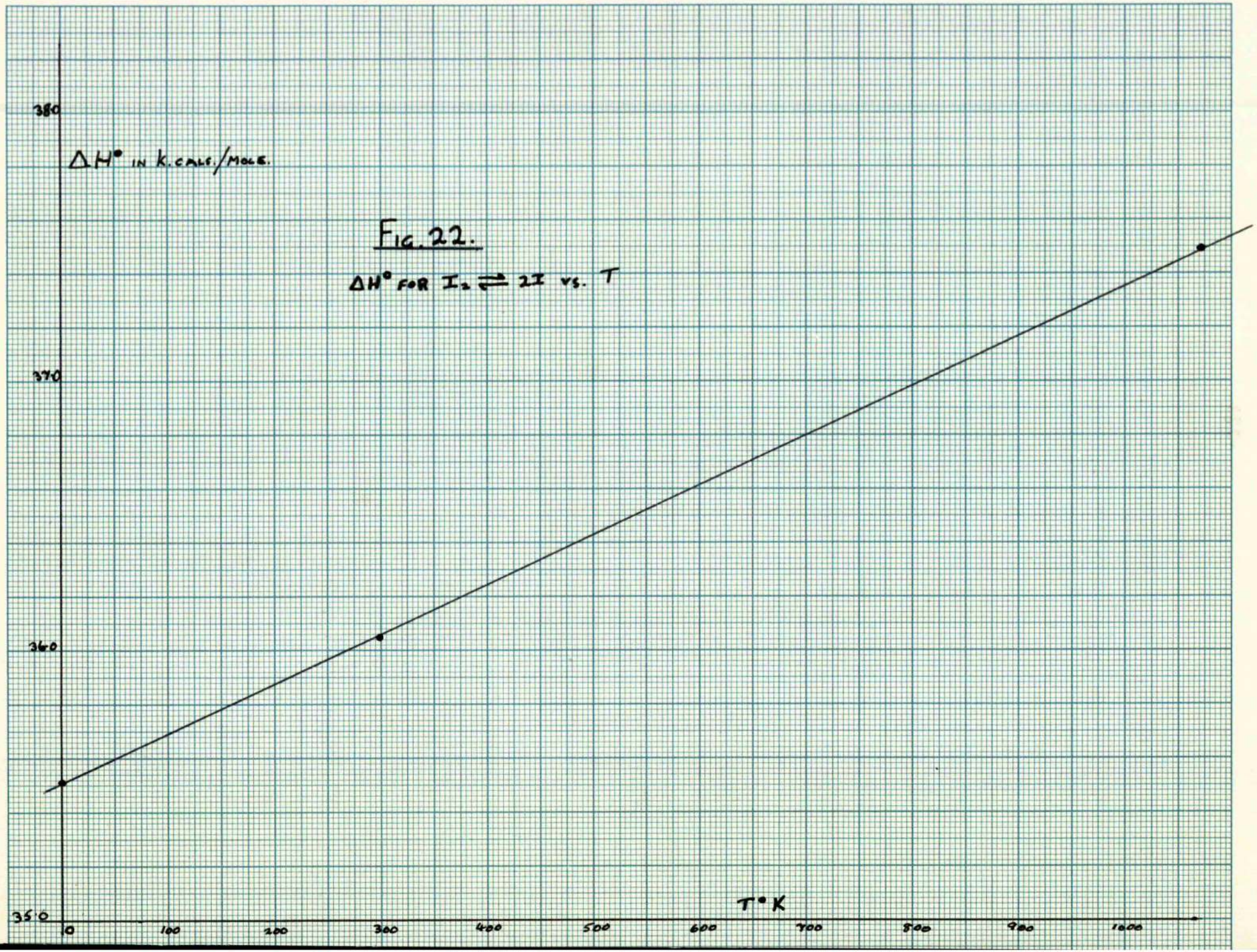


FIG. 22.

ΔH° FOR $I_2 \rightleftharpoons 2I$ VS. T

APPENDIX V

The Variation of the Iodine Dissociation Equilibrium Constant with Temperature.

From the data of Perlman and Rollefson[69], the value of ΔH° for the reaction

$$I_2 \longrightarrow I + I$$

over the range 872°K to 1274°K can be derived to be 37,500 cals./mole, if it is assumed that ΔH° is constant over this range. If this value is ascribed to their median temperature, then

ΔH°_{1073} = 37,500 cals./mole.

They also give ΔH°_{298} = 36,057 cals./mole.

ΔH°_{o} = 35,514 cals./mole.

This variation of ΔH° with temperature is shown in Fig. 22. Since a straight line is obtained, then,

$$\frac{d\,(\Delta H^{\circ})}{dT} = \text{constant},$$

so that $\Delta H^{\circ}_{T} = \Delta H^{\circ}_{o} + aT$, where $\underline{a}$ is a constant.

Therefore, on integration of the equation

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^{\circ}}{RT^2},$$

we obtain $\ln K = -\frac{\Delta H^{\circ}_{o}}{RT} + \frac{a}{R} \ln T + I,$

where I is an integration constant.

That is, $\log K_p + \frac{\Delta H^{\circ}_{o}}{4.57\,T} = b.\log T + J,$

where R x ln 10 = 4.57, $b = \frac{a}{R}$, $J = I \div \ln 10$,

and K_p is the iodine dissociation constant in atmospheres.

Thus, there should be a linear relationship between the expression on the left-hand-side of this equation and log T. The data of Perlman and Rollefson were fitted to this equation statistically, putting ΔH_o^o = 35,514 cals/mole. This gave

$$\log K_p + \frac{35,514}{RT} = (0.907 \pm 0.062) \log T + (2.556 \pm 0.003).$$

$$\text{i.e. } \log K_p = -\frac{7,788}{T} + (0.907 \pm 0.062)\log T + 2.556,$$

neglecting errors in the constant term.

Since the rate-constants derived from the present experimental data are in concentration units, an expression for Kc is required.

$$\text{Since } K_p = p_I^2/p_{I_2} = \frac{[I]^2 . [RT]^2}{[I_2] . RT} = Kc.(RT).,$$

then log Kc = log Kp - log RT

$$\text{That is, } \log Kc = -\frac{7,788}{T} + 0.907 \log T + 2.556 - \log RT$$

$$= -\frac{7,788}{T} + \log T\,(0.907 - 1.0) + 2.556 - \log 0.08205$$

$$\text{i.e. } \log Kc = -\frac{7,788}{T} - 0.093 \log T + 3.622, \text{ where}$$

Kc is in moles/litre.

The coefficient b of log T in the expression given above for $\log K_p$ is shown to be identical with $\frac{a}{R}$, where

$$\Delta H_T^o = \Delta H_o^o + aT.$$

Then, since $\underline{b} = 0.907 \pm 0.062$, then $\underline{a} = 1.798 \pm 0.125$,

so that $\Delta H^{\circ}_{T} = \Delta H^{\circ}_{o} + (1.798 \pm 0.125)\ T$.

Then, at the median temperature of the present range, 568°K,

$$\Delta H^{\circ}_{568} = 55{,}514 + (1.798 \times 568) \pm (0.125 \times 568)$$

$$= 56{,}535 \pm 69.9 \text{ cals/mole.}$$

i.e.

$$\Delta H^{\circ}_{568} = 56{,}540 \pm 70 \text{ cals/mole.}$$

This error in the value of ΔH° is negligible compared to that in $E_{exp.}$

APPENDIX VI

Correction to 0°K of ΔH° for the reaction $I + CH_3I \rightarrow CH_3 + I_2$.

For each reactant and product, the value of $H^\circ_{568} - H^\circ_o$ is required. Treating iodine atoms as a perfect monatomic gas, $C_p = C_v + R = \frac{5}{2}.R$, and since in this case, $\Delta H_1^2 = C_p(T_2-T_1)$, then

$$H^\circ_{568} - H^\circ_o = \frac{5}{2}R \times 568 \text{ cals/mole} = 2.81 \text{ k. cals/mole.}$$

Values of thermodynamic functions have been calculated from spectroscopic data by Fenlon, Cleveland and Meister[77] for CH_3I. Interpolation gives $H^\circ_{568} - H^\circ_o = 6.04$ k. cals/mole.

Thus, $H^\circ_{568} - H^\circ_o$ for the reactants is 8.85 k.cals/mole. Murphy[78] has conveniently derived power series in T for the various thermodynamic functions of a range of simple molecules, including iodine. On inserting T = 568 into the appropriate formula, $H^\circ_{568} - H^\circ_o = 4.82$ k. cals/mole for I_2.

All the above values should be fairly accurate. The case of the methyl radical is more uncertain. The value of $H^\circ_{568} - H^\circ_o$ for methane is 5.21 k. cals/mole, from the tables compiled by Pitzer.[79] Kistiakowsky and Van Artsdalen[72] estimated $H^\circ_{568} - H^\circ_o$ for a methyl radical at 455°K by diminishing the value for methane by 0.5 times the vibrational contribution, which amounted to about 0.09 k. cals./mole.

A detailed calculation of the vibrational contribution at 568°K was not made. An arbitrary correction of 0.12 k. cals/mole was

subtracted from the value for methane, giving $H^{\circ}_{568} - H^{\circ}_{o}$ for a methyl radical as 5.09 k. cals/mole. The error involved here is likely to be small, and in any case negligible compared with the experimental error in the activation energies.

Thus, $H^{\circ}_{568} - H^{\circ}_{o}$ for the products is 9.91 k. cals/mole, and $\Delta(H^{\circ}_{568} - H^{\circ}_{o})$ = (9.91 - 8.85) k. cals/mole. = 1.06 k.cals/mole.

In the same way, values of $H^{\circ}_{298} - H^{\circ}_{o}$ can be calculated to be:-

I, 1.48; CH_3I, 2.58; CH_4, 2.40; CH_3, 2.35; I_2, 2.42; all in k. cals per mole.

Hence $\Delta(H^{\circ}_{298} - H^{\circ}_{o})$ for reaction (1) is 0.7 k. cals/mole.

APPENDIX VII

Collision Theory calculation of A-factor for reaction (1).

According to classical collision theory, $-\frac{dn}{dt} = Z_{1,2}\ e^{-E/RT}$,

where $-\frac{dn}{dt}$ is the reaction rate in terms of the number of molecules of one reactant removed by reaction per cc. per second, and $Z_{1,2}$ is the bimolecular collision rate.

Thus, $-\frac{dn}{dt} = n_1\ n_2\ \pi\left(\frac{d_1 + d_2}{2}\right)^2 \sqrt{\frac{8kT}{\pi\mu}} \times e^{-E/RT}$, where

n_1, n_2 are the numbers of molecules/cc. present of species 1 and 2, d_1, d_2 are their respective collision diameters, and μ is the reduced mass $= \frac{m_1\ m_2}{m_1 + m_2}$.

Experimentally, $-\frac{dc}{dt} = k_{exp.} c_1\ c_2 = A\ e^{-E/RT}\ c_1\ c_2 = \frac{dx}{dt}$,

where, in the present example, $c = c_1$ = concentration of CH_3I in moles/litre, x = concentration of I_2, and c_2 = concentration of I atoms.

In order to equate the two expressions for the rate, and thus derive a theoretical value for A in terms of molecular parameters, the units used must be made the same.

Thus, $-\frac{dn}{dt} \times \frac{1000}{N} = -\frac{dc}{dt}$, both being in units of moles litres^{-1} seconds^{-1}.

Also, putting $c_1 = \frac{n_1 \times 1000}{N}$, and $c_2 = \frac{n_2 \times 1000}{N}$,

$$\frac{1000}{N} \times n_1 n_2\ \pi\left(\frac{d_1 + d_2}{2}\right)^2 \sqrt{\frac{8kT}{\pi\mu}} = A\ n_1\ n_2 \left(\frac{1000}{N}\right)^2,$$

whence $A = \frac{N}{1000} \times \pi \left(\frac{d_1 + d_2}{2}\right)^2 \times \sqrt{\frac{8kT}{\pi\mu}}$ litres moles^{-1} seconds^{-1}.

On inserting $N = 6.025 \times 10^{23}$, $d_1 = d_I = 3.5$ A$^\circ$, $d_2 = d_{CH_3I}$ $= 5.1$ A$^\circ$, $m_1 = 127$ a.w.u., $m_2 = 142$ a.w.u., $k = 1.380 \times 10^{-16}$ ergs/degree, the value of A is found to be 5.5×10^{12} litres moles^{-1} seconds^{-1}.

The value found experimentally was $10^{10.71}$ litres moles^{-1} seconds^{-1}, so the P- factor is of the order of 10^{-2}.

APPENDIX VIII

Evaluation of entropy of activation for reaction (1) from the experimentally determined A- factor.

Reaction (1) is the elementary reaction $I + CH_3I \longrightarrow CH_3 + I_2$.

The bimolecular rate constant k_1 has been determined experimentally as $10^{10.71} \; e^{-19,200/RT}$. This assumes that, over the temperature range investigated, the temperature dependence of k_1 is given by the Arrhenius equation $k_1 = A_1 \cdot e^{-E_1/RT}$.

$$\text{i.e.} \quad \frac{d \ln k_1}{dT} = \frac{E_1}{RT^2}$$

From transition state theory,

$k_1 = \frac{kT}{h} \; e^{\Delta S_c^*/R} \; e^{-\Delta H^*/RT}$, assuming the transmission coefficient is unity, where ΔH^* is the enthalpy of activation, and ΔS_c^* the entropy of activation for a standard state of 1 mole/litre.

Writing this as $\ln k_1 = \ln k/h + \ln T + \ln K_c^*$, and differentiating,

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2} = \frac{1}{T} + \frac{\Delta E^*}{RT^2}$$

$$\text{i.e.} \quad E_1 = RT + \Delta E^* = RT + \Delta H^* - P.\Delta V^*$$

$$= RT + \Delta H^* - \Delta n^*. RT.$$

$$\text{Thus,} \quad \Delta H^* = E_1 - (1 - \Delta n^*)RT.$$

Inserting this value for ΔH^* into the transition state expression

for k_1 gives $k_1 = \frac{kT}{h} \; e^{\Delta S_c^*/R} \; . \; e^{1-\Delta n^*} \; . \; e^{-E_1/RT}$

By comparing this with the Arrhenius expression $k_1 = A_1 . e^{-E_1/RT}$,

$A_1 = \frac{kT}{h} \; e^{\Delta S_c^*/R} \; e^2$., since for reaction (1), $\Delta n^* = -1$,

two reactant species coalescing to form the transition complex.

Then, $\ln A_1 = \ln \frac{kT}{h} + 2 + \Delta S_c^*/R.$

Thus, $\Delta S_c^* + 2R = R(\ln A_1 - \ln \frac{kT}{h})$

$= 4.57 \; (\log A_1 - \log \frac{kT}{h})$

Putting $\log A_1 = 10.71$, (as determined experimentally), $T = 568^{\circ}K$, $k = 1.380 \times 10^{-16}$ ergs/degree, and $h = 6.625 \times 10^{-27}$ erg - seconds, gives $\Delta S_c^* + 2R = -10.79$ cals/degree, whence $\Delta S_c^* = -14.75$ cals/degree, for a standard state of 1 mole/litre.

APPENDIX IX

Theoretical Estimation of Entropy of Activation for reaction (1),

$I + CH_3I \longrightarrow CH_3 + I_2$.

The entropies of the species CH_3I, I, and the transition complex CH_3I_2, must be estimated in the gas-phase at 568°K.

(a) CH_3I

$S^\circ_{trans} = R(\frac{5}{2} \ln T + \frac{3}{2} \ln M - \ln P - 1.164)$, for a standard state of 1 atmosphere, where M is the molecular weight and P the pressure in atmospheres. (Sachur - Tetrode Equation).

Thus, for T = 568°K, M = 142, P = 1,

$S^\circ_{trans} = 45.91$ cals/degree

$S^\circ_{rot.} = R(\frac{3}{2} \ln T + \frac{1}{2} \ln ABC - \ln \sigma) - 5.384$, where A,B,C are the principal moments of inertia in units of atomic-weight-units - $Å^2$, and σ is the symmetry number.

For CH_3I, $\sigma = 3$, corresponding to the three equivalent positions of the hydrogen atoms on rotating the molecule about the carbon-iodine axis. The values of A, B and C used were those determined by Gordy, Simmons and Smith.[80] Thus A = 3.31, B = C = 67.34, both in a.w.u. $Å^2$.

Then $S^\circ_{rot.} = 20.86$ cals/degree.

$$S^\circ_{vib.} = -R \sum_i d_i \ln(1-e^{-\omega_i hc/kT}) + R \frac{hc}{kT} \cdot \sum_i \frac{d_i \omega_i e^{-\omega_i hc/kT}}{1 - e^{-\omega_i hc/kT}}$$

$$= -\frac{F}{T} + \frac{H}{T}$$

A spectroscopic analysis of methyl iodide has been carried out by Fenlon, Cleveland and Meister.[77] Using the values derived by them for the nine (=3n-6) fundamental frequencies, the corresponding functions for $-\frac{F}{T}$ and $\frac{H}{T}$ are readily obtained from the tables published by Wilson.[81]

ω_i	$\frac{\omega_i}{T}$	d_i	$-\frac{F^o}{T}$	$\frac{H^o}{T}$	$\frac{S^o}{d_i}$	S^o
3000	5.5	1	.001	.008	.009	.009
1250	2.20	1	.087	.280	.367	.367
550	0.97	1	.570	.916	1.486	1.486
3050	5.4	2	.001	.007	.008	.016
1450	2.55	2	.052	.195	.245	.490
900	1.58	2	.218	.522	.740	1.480

The values of ω_i are in wave-numbers, ($cms.^{-1}$), and the temperature T = 568°K. The total $S^o_{vib.}$ is the sum of the entries in the final column, i.e. $S^o_{vib.}$ = 5.85 cals/degree.

Then, for CH_3I, $S^o_{total} = S^o_{trans.} + S^o_{rot.} + S^o_{vib.}$

= 68.62 cals/degree.

(b). I

If iodine atoms are treated as an ideal monatomic gas, then $S^o_I = S^o_{trans} + S^o_{el.}$, where $S^o_{el.}$ is the contribution to the entropy of the unpaired electron. This is discussed more fully at the end of this section.

$S^{\circ}_{trans.} = R\left(\frac{5}{2} \ln 568 + \frac{3}{2} \ln 127 - \ln 1 - 1.164\right)$

$= 45.58$ cals/degree.

Then S°_{total} for I $= 43.58 + S^{\circ}_{el.}$ cals/degree.

Then $\Sigma S^{\circ}_{reactants} = 112.20 + S^{\circ}_{el.}$ cals/degree.

(c). $\underline{CH_5I_2}$

$S^{\circ}_{trans.} = R\left(\frac{5}{2} \ln 568 + \frac{5}{2} \ln 269 - \ln 1 - 1.164\right) = 45.82$ cals/degree.

In order to evaluate $S^{\circ}_{rot.}$ and $S^{\circ}_{vib.}$, the spatial dimensions and fundamental frequencies of the transition complex must be guessed.

It seems reasonable to assume that the complex is linear with respect to the carbon and iodine atoms. Also, it is readily shown that the centre of gravity of the methyl groups lies on the C - I - I axis at a point 0.02 Å from the carbon nucleus, and substitution of a point mass of 15 a.w.u. at this point for the methyl group simplifies the calculation of the rotational contribution.

The moment of inertia about the C - I - I axis is due only to the hydrogen atoms, and is thus very small compared with the other moments of inertia. Thus, no appreciable error is involved in assuming that it has the same value as in CH_3I, i.e. 5.31 a.w.u. Å ^{2}.

Bond lengths in the transition complex must now be assigned. The following normal bond lengths are taken from the Tables edited by Sutton.[82]

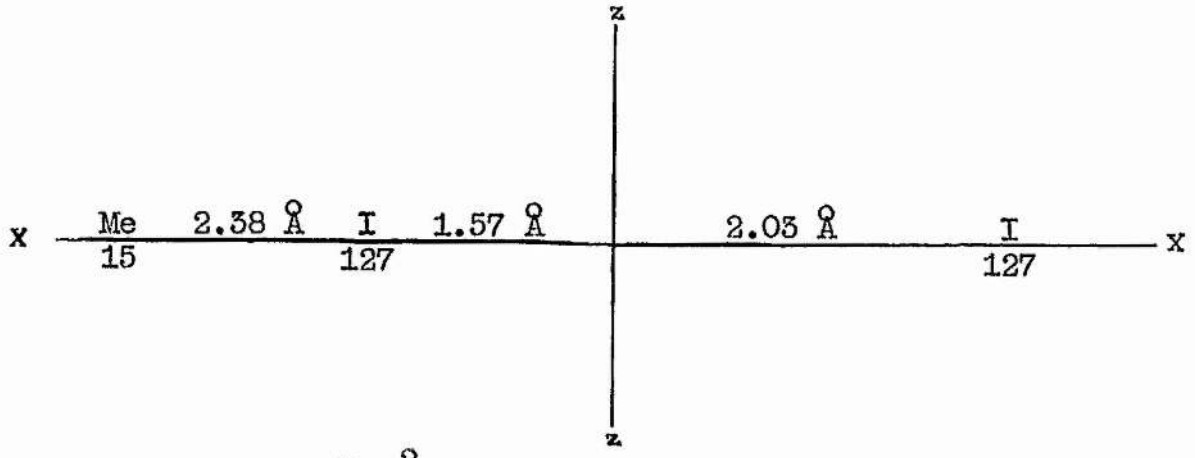
C - H 1.09 Å in CH_4

H - Br 1.41 Å

C - I 2.16 Å in CH_3I

I - I 2.66 Å

For the analogous transition complex CH_4Br, Kistiakowsky and Van Artsdalen[72] assigned bond distances C - H = 1.17 Å and H - Br = 1.86 Å , along the reaction coordinate. These values correspond to 7% and 32% extensions of the normal bond lengths, respectively. Since the C - I and I - I bonds are likely to be more readily extended than the C - H and H - Br bonds respectively, the percentage extensions will probably be larger. The C - I bond was assigned the length 2.56 Å, and the I - I bond 5.60 Å. If the centre of gravity is chosen as the origin, the system is readily shown to correspond to that shown:-



Then $I_{zz} = I_{yy} = \Sigma mx^2$

$= 15(2.38 + 1.57)^2 + 127(1.57)^2 + 127(2.05)^2$

$= 1069.7$ a.w.u. Å ^{2}.

Then $S^{\circ}_{rot.} = R\left(\frac{3}{2} \ln 563 + \frac{1}{2} \ln 5.5 \times 1069.7^2 - \ln 3\right) - 5.584$

$= 26.44$ cals./degree

It is reasonable to assume that the methyl group can rotate freely about the x x axis, so there is no contribution from this type of motion.

Since the complex contains 6 atoms, and is non-linear, it must possess 12 normal vibrational modes. The frequencies assigned were those determined for methyl iodide, diminished by a quantity arrived at by pure guesswork to account for the electron-deficiency of the entity, which will tend to weaken the bonds. The three additional frequencies were assigned by analogy with those assigned for CH_4Br,[72] taking into account the large mass of the iodine atoms and the fundamental frequency of the iodine molecule.[85] The frequencies assigned, and their contributions to the entropy, as determined from the tables of Wilson,[81] are tabulated below. (The method assumes that the oscillations are harmonic).

ω_i for CH_3I,	ω_i for CH_3I_2,	di	$\frac{\omega_i}{T}$	$\frac{H^{\circ}}{T}$	$-\frac{F^{\circ}}{T}$	$\frac{S^{\circ}}{d_i}$	S°
3000	2900	1	5.1	.010	.001	.011	.011
1250	1150	1	2.02	.337	.113	.450	.450
550	450	1	0.79	1.070	.774	1.844	1.844
3050	2950	2	5.2	.009	.001	.010	.020
1450	1550	2	2.58	.252	.067	.299	.598
900	800	2	1.41	.614	.285	.897	1.794
I-I stretch	150	1	0.26	1.640	2.521	5.961	5.961
Me-I-I bend	100	2	0.18	1.742	2.944	4.686	9.372

The ω_i are in cms^{-1}, and T = 568°K. The total $S^\circ_{vib.}$ is the sum of the figures in the final column. The transition state theory requires one vibrational mode to be omitted, this corresponding to the reaction coordinate. The C - I stretching mode would seem to be the logical choice, and it seems probable that this can be identified as the third in the above table, with $\omega = 450\ cms^{-1}$.

Thus, $S^\circ_{vib.} = 16.21$ cals/degree.

Then, $S^\circ_{total} = S^\circ_{trans.} + S^\circ_{rot.} + S^\circ_{vib.} + S^\circ_{el.}$

$= 88.47 + S^\circ_{el.}$ cals./degree.

Thus, $\Delta S^\circ_P = 88.47 - 112.20 + \Delta S^\circ_{el.}$ cals/degree.

$= -25.75 + \Delta S^\circ_{el.}$ cals./degree, for a standard state of 1atmosphere.

For comparison with the value derived from the experimental data, this must be converted to a standard state of 1 mole per litre. It can be shown that

$\Delta S^\circ_c = \Delta S^\circ_P - \Delta n.R.\ln RT$, where (RT) is in litres atmospheres

Since for reaction (1), $I + CH_3I \longrightarrow CH_3I_2 \longrightarrow$ products,

$\Delta n = -1$, then $\Delta S^\circ_c = \Delta S^\circ_P + 4.57.\ \log\ (0.08205 \times 568)$

$= -25.75 + 7.62 = -16.11$ cals./degree.

To this must be added $\Delta S^\circ_{el.}$ The energy separation between electronic states is usually so great that at ordinary temperatures only one state, the lowest, is occupied. The electronic partition function $Qe = \sum_i g_i\ e^{-Ei/kT} = g_1$ if only state 1 is occupied, since E_1 is taken as zero.

The degeneracy g of an electronic state is 2J + 1, where J is the resultant quantum number, or total angular momentum quantum number.[84] The ground state of an iodine atom is a $^2P_{3/2}$ state, so that $J = \frac{3}{2}$ and g = 4. The next highest state, $^2P_{\frac{1}{2}}$, lies 7,603 cms^{-1} above the ground state,[85] so that hcw/kT = 19.5 at 568°K. Thus, the contribution to the electronic partition function of this level is $2 \times e^{-19.5}$, which is negligible, so the electronic entropy of iodine atoms is R ln 4 cals./degree. That the ground state only should be considered is not a general rule is exemplified by the case of chlorine atoms, for which the $^2P_{\frac{1}{2}}$ state is only 881 cms.$^{-1}$ above the ground $^2P_{3/2}$ state,[85] and must be taken into consideration.[75] Thus, the general rule stated by Trotman-Dickenson,[86] that the electronic entropy of free radicals and atoms is always R ln 2, should be used with care.

The electronic entropy of the CH_3I_2 radical is difficult to estimate. Pitzer[75] assigned only electronic spin entropy R ln 2 to the analogous transition complex CH_3-H-Cl involved in the chlorination of hydrocarbons. If the same assignation is made for the CH_3-I-I activated complex, then, in the present case, S^*_{el} = R ln 2 - R ln 4 = - 1.38 cals./degree. It should be noted that this change in electronic entropy does not imply that reaction (1) is non-adiabatic in the sense used by Glasstone, Laidler and Eyring,[87] i.e. there is no change in S_1 the total electron spin, which is $\frac{1}{2}$ for iodine atoms and for methyl radicals. (According to Mulliken,[76] the ground state of a methyl radical is represented by a term $^2A_1$ or $^2A_2$[11], where the

superscript 2 denotes the value of $2S + 1$, so $S = \frac{1}{2}$. The other symbols used do not have interpretations analogous to those used to describe atomic and diatomic molecular terms). The non-zero electronic entropy change is due to the fact that the degeneracy factor g $= 2J + 1$, not $2S + 1$, and that it is the latter which must remain invariant.

Thus, the estimated theoretical entropy of activation for reaction (1) is-16.11 - 1.38 = 17.49 cals./degree, for a standard state of 1 mole per litre.

The possible errors arise from ignorance of the appropriate parameters of the transition complex. Thus, the translational contribution is accurately known, to within the validity of the ideal gas laws, while the errors made in guessing the principal moments of inertia are probably not very great. The main uncertainty lies in the assignation of fundamental frequencies to the complex. The vibrational contribution is fairly large in the present instance, as the large mass and relatively weak covalent binding power of the iodine atoms introduce relatively low frequencies, which would be appreciably excited at the experimental temperature. The nuclear spin contributions have been ignored, as they cancel out, and the electronic contribution is fully discussed above. The twin assumptions that polyatomic molecules act simultaneously as rigid rotators and simple-harmonic oscillators are, of course, mutually exclusive, but are commonly made.

APPENDIX X

Estimation of $\Delta S^{\circ}_{1.2}$ and $\Delta S^{\circ}_{5.5}$ at 298°K, where $\Delta S^{\circ}_{1.2}$ is the entropy change for the proces (1,2) below, $\Delta S^{\circ}_{5.5}$ that for (5,5).

$\underline{\Delta S^{\circ}_{1.2}}$ $\qquad I + CH_3I \underset{2}{\overset{1}{\rightleftharpoons}} CH_3 + I_2$

S°_{298} for CH_3I = 60.7 cals./degree.[77]

S°_{298} for I = $S^{\circ}_{trans.} + S^{\circ}_{el.}$

= R(2.5 ln 298 + 1.5 ln 127 - 1.164) + R ln 4 (See Appendix IX)

= 43.2 cals./degree.

S°_{298} for I_2 - calculated by power series in T given by Murphy,[78]

= 62.5 cals./degree.

S°_{298} for CH_3. The entropies of various models for the CH_3 radical have been estimated as follows[88]:-

Planar, symmetry number 6, S° = 44.0

Non-planar, symmetry number 3, high inversion frequency, S° = 44.1

Non-planar, symmetry number 3, very low inversion frequency, S° = 45.5

These values do not include the electronic contribution, and have an estimated uncertainty of not more than ± 1 cal./degree. The favoured value appears to be 45.5 cals./degree, which along with electronic entropy R ln 2, (See Appendix IX), gives S°_{298} = 46.9 cals./degree, for CH_3.

Then, $(\Delta S^{\circ}_{p})_{1.2}$ = (46.9 + 62.5) - (60.7 + 45.2)

= 5.5 cals./degree.

Now, since $\Delta S^{o}_{c} = \Delta S^{o}_{p} - \Delta n.R.\ln RT$, and $\Delta n = 0$, then

$(\Delta S^{o}_{c})_{1.2} = (\Delta S^{o}_{p})_{1.2} = 5.5$ cals./degree at 298°K.

$\underline{\Delta S^{o}_{5.5}}$ $\quad CH_5 + HI \underset{5}{\overset{5}{\rightleftharpoons}} CH_4 + I$

S^{o}_{298} for CH_4 = 44.5 cals./degree.[79]

S^{o}_{298} for I = 45.2 cals./degree.(See above).

S^{o}_{298} for CH_5 = 46.9 cals./degree.(See above).

S^{o}_{298} for HI = 49.7 cals./degree, calculated from formula given by Murphy.[78]

Then $(\Delta S^{o}_{c})_{5.5} = (\Delta S^{o}_{p})_{5.5} = (44.5 + 45.2) - (46.9 + 49.7) =$

-8.9 cals./degree. at 298°K.

APPENDIX XI

Evaluation of Experimental and Theoretical Entropies of Activation for Reaction (5) at 570° K.

$$I + CH_4 \longrightarrow CH_3 + HI \quad (5)$$

$\Delta S^*_{exp.}$

A_5 has been determined as $10^{10.60}$ litres moles^{-1} secs^{-1} at 298°K

$= 10^{13.60}$ ccs. moles^{-1} secs^{-1} at 298°K

$= 10^{13.74}$ ccs. moles^{-1} secs^{-1} at 570°K,

assuming the value of A_5 varies with $T^{\frac{1}{2}}$.

From transition state theory, (see Appendix VIII),

$A = kT/h \cdot e^2 \cdot e^{\Delta S^*/R}$, so that

$\Delta S^*_5 = 4.57(\log A_5 - \log kT/h) - 2R$

$= -0.91$ cals./degree at 570°K, for a standard state of 1 mole/cc.

ΔS^* theor.

S°_{570} for I = $S^\circ_{trans.} + S^\circ_{el.}$ = 45.6 + 2.8 (See Appendix IX)

= 46.4 cals./degree.

S°_{570} for CH_4 = 51.5 cals./degree, by interpolation of data tabulated by Pitzer.[79]

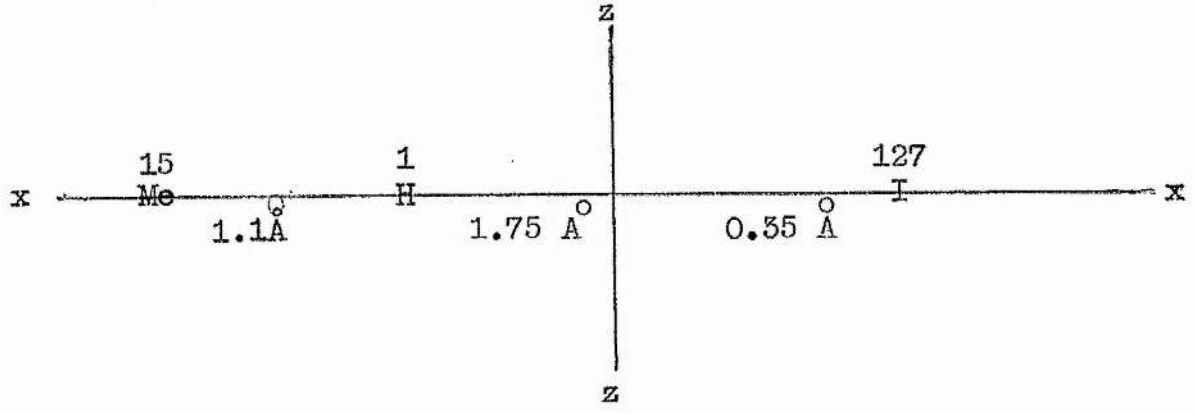
Thus ΣS°_{570} for reactants = 97.7 cals./degree.

CH_4I :- $S^\circ_{trans.} = R(2.5 \ln 570 + 1.5 \ln 143 - 1.164) = 45.9$ cals./degree.

The complex is assumed to have a linear configuration, with

bond distances H_5C —1.17 Å— H —2.11 Å— I, by analogy with those assigned to the CH_4Br complex by Kistiakowsky and Van Artsdalen.[72] The CH_5 group can be considered as a mass of 15 a.w.u. on the C-H-I axis, 0.02 Å from the carbon nucleus. (See Appendix IX). Also, the moment of inertia around the C-H-I axis, due only to the hydrogen atoms of the methyl group, will be small, and approximately equal to the corresponding value for methyl iodide,[80] viz. 5.31 a.w.u. Å^2.

Then, taking the centre of gravity as origin, the system is readily shown to be equivalent to that shown.



$$I_{zz} = I_{yy} = 15(1.1 + 1.75)^2 + 1\ (1.75)^2 + 127(0.35)^2$$
$$= 207.6 \text{ a.w.u. Å}^2$$

Then $S^\circ_{rot.} = R\left(\frac{3}{2} \ln 570 + \frac{1}{2} \ln 5.31 \times 207.6 \times 207.6 - \ln \sigma\right) - 5.384$, where $\sigma = 3$ is the symmetry number, so $S^\circ_{rot.} = 25.1$ cals./degree.

To evaluate $S^\circ_{vib.}$, the fundamental frequencies must be assigned to the complex. Since the purpose of this calculation is to compare the result with that obtained by Kistiakowsky and Van Artsdalen,[72]

for the analogous reaction $Br + CH_4 \longrightarrow CH_3 + H\,Br$, frequencies were assigned to the present complex so as to correspond to those made for the CH_4Br complex. The frequencies assigned, in cms.$^{-1}$, are shown in the table below, together with the required functions evaluated from the tables of Wilson[81]:-

ω	$\frac{\omega}{570}$	g	H^o/T	F^o/T	S^o/g	S^o
5000	5.3	3	.008	.001	.009	.027
2000	4.7	1	.016	.002	.018	.018
300	0.53	2	1.327	1.254	2.581	5.162
1440	2.53	5	.197	.053	.250	1.250

The frequency corresponding to the H - I stretching mode has been omitted, as this has been chosen as the reaction coordinate. Then $S^o_{vib.}$ is the sum of the last column = 6.5 cals./degree.

If the electronic entropy is taken to be R ln 2 = 1.4 cals./degree, (See Appendix IX), then S^o_{total} for the transition complex CH_4I

$= S^o_{trans.} + S^o_{rot.} + S^o_{vib.} + S^o_{el.} = 74.9$ cals./mole.

Then, $\Delta S^*_P = 74.9 - 97.7 = -22.8$ cals./degree at 570°K, for a standard state of 1 atmosphere.

Now $\Delta S^*_c = \Delta S^*_P - \Delta n\, R \ln P.\ \Delta V^*$, where $\Delta n = -1$ in the present case, and ΔV^* is the volume change at the appropriate temperature (570°K) and pressure (1 atmosphere). Since ΔS^*_c is required relative to a standard state of 1 mole/cc., ΔV^* should be expressed in ccs.

Then ΔS^*_o = - 22.8 + R ln (1 x 22,400 x 570/273)

= - 1.5 cals./degree at 570°K, for a standard state of 1 mole/cc.

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